SOME FUNDAMENTAL PROBLEMS IN CHEMISTRY—OLD AND NEW

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PREFACE

When the manuscript of this book was finished it was submitted to my old friend Sir William Ramsay for his opinion, when he was so good as to express his entire approval of it and suggested later that as he had undertaken to write a book on somewhat similar lines for "Harper's Library of Living Thought" we might collaborate if I was willing to do so. To this I gladly agreed, but as the joint work proceeded it became evident that while there was much in common in our treatment of the subjects discussed, we approached them from somewhat different points of view. This I pointed out and suggested that as it did not seem possible without one of us entirely re-writing the whole of his part of the joint work, to weld the two divisions into a harmonious whole, it might be simpler for each of us to return to the original plan and to proceed independently of each other—a proposition to which Sir William at once agreed.

I mention this matter because inadvertently in his book for the Harper series, "Elements and Electrons," the chapter on the Atomic Theory contains a page or two of my original manuscript on the same subject, and I have his permission for stating that this occurred through a pure accident on his part.

Regarding the general plan of this book, I have very little to say, as its essence is embodied in the title.

I may however mention that one of my chief ideas was to contrast certain ancient views, such as those of atoms and a primordial element or primordial elements in the shape of air, earth, fire and water, together with the possibility of transformations of these latter into each other, with the modern conception of electrons and the discovery of changes, such as

those which the radio-active elements experience, which amount in point of fact to a change of one so-called chemical element into others, these two modern discoveries proving first as Ladenburg has said, "*Dass unter den Griechen und Römern Männer waren, die sich in jeder Beziehung mit unseren Denkern messen konnten,*" and secondly that even in Science history may repeat itself.

I have therefore discussed the ancient views regarding the nature of matter and the Atomic Theory (involving as it does questions like that of the Periodic Law) at some length and also the subject of Radio-activity in a similar manner.

The latter is no doubt as yet in its infancy and our knowledge of it is, it may be said, changing from day to day. I have however given as far as possible the latest available information, for which I have relied largely on Rutherford's "Radio-active Substances and their Radiations," which was published in October, 1912.

It is only right that in this connection I should express my thanks to Dr. Robert Jack, of this University, who spent much time and labour in revising the proofs dealing with that branch of the subject and who supplied me with many valuable hints and much useful information. Regarding the two last chapters on the question of Inorganic Evolution and Arrhenius' views on "Worlds in the Making" respectively, both deal with questions of fundamental interest and importance in relation to matter and energy, and neither appear to have been presented to the student in a condensed form.

I can only hope that my efforts in this direction have been successful.

It only remains for me to express my thanks to quite a number of individuals whose kind assistance has placed me under considerable obligations.

My old friends (and former pupils) Professors Collie and Donnan were so kind as to read through the manuscript and to make many valuable suggestions.

Dr. A. W. Stewart and Mr. A. Killen Macbeth have been most kind in revising the proofs and in other ways, and Miss Florence Rea assisted me in drawing up the new curve of Atomic volumes.

Professor Svante Arrhenius was so good as to read over the last two chapters of the book and to suggest two valuable notes. Finally I have also to thank him for granting me permission to reproduce some of the illustrations from his work "Worlds in the Making," and Messrs. Harper and Brothers, who hold the English rights in these, were also so kind as to consent to the reproductions.

Similarly Sir Norman Lockyer has permitted me to reproduce certain illustrations from his work on "Inorganic Evolution" and Messrs. Macmillan (his publishers) were so good as to grant permission also.

Mr. Strutt, in like manner, permitted me to make use of one of the illustrations from his "Becquerel Rays."

I desire to express my indebtedness to these gentlemen also.

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CHAPTER I

THE OLDER CHEMISTRY

ANCIENT THEORIES REGARDING THE NATURE OF MATTER AND MORE RECENT THEORIES AS TO THE NATURE OF ENERGY.

There is an inborn tendency in the human mind to inquire into the ultimate nature of things, and, if no immediate explanation is forthcoming, to frame an hypothesis or theory on the matter. This tendency has probably existed since man acquired reasoning powers, and it was certainly highly developed among the early Greeks.

"It is the distinguishing peculiarity of the Greeks that they were the only people of the ancient world who were prompted to assume a scientific attitude in explaining the mysteries which surrounded them. They were the first and the only people who disengaged speculation from theological guidance. . . . The early Greek had no predecessor from whom to learn. He found himself in the presence of mysteries which he vainly endeavoured to explain by polytheistic agencies. He not only saw reason to disbelieve in these agencies, but saw that if they existed, their arbitrary and inscrutable volitions rendered all explanation and prediction impossible.

"He sought elsewhere. Thales and the other Ionic thinkers fixed upon common agencies—water, fire, air, etc., and tried to reconstruct the world out of these. . . . The great fact respecting this first epoch is that the belief in the phenomena of nature as brought about by the

volition of numerous unseen beings was quietly set aside: the causes of all change were sought in the conditions of things themselves."[1]

It was in this way that the early Greek philosophers came to speculate on the ultimate nature of matter.

Thales[2] opened the inquiry:—

"He felt that there was a vital question to be answered relative to the beginning of things. He looked around him, and the result of his meditation was the conviction that moisture was this beginning. He was impressed with this idea by the earth. There he found moisture everywhere. All things he found nourished by moisture: warmth itself he declared to proceed from moisture: the seeds of all things are moist. Water when condensed becomes earth.

"Thus convinced of the universal presence of water, he declared it to be the beginning of things.

"Thales would all the more readily adopt this notion from its harmonising with ancient opinions; such, for instance as those expressed in Hesiod's "Theogony"—wherein Oceanus and Thetis are regarded as the parents of all such deities as had any relation to nature. He would thus have performed for the popular religion that which modern science has performed for the book of Genesis."[3]

Following Thales in the idea of a single primordial principle or element, Anaximenes[4] maintained that such principle was air and not water.

Heraclitus[5] was of the opinion that it was neither of these, but fire, while lastly, in relation to a single element theory Pherekides[6] maintained that it was earth.

Empedocles[7] introduced the idea of four distinct elements, namely, those just mentioned, earth, air, fire and water, which were capable of forming all things by their intermixture.

These elements he believed were acted upon by the forces of

[1] Lewis, "History of Philosophy."
[2] Born about 640 B.C.
[3] Lewis, *loc. cit.*
[4] Born about 550 B.C.
[5] Born about 503 B.C.
[6] Born about 6 B.C.
[7] Born about 384 B.C.

love and hatred: the former causing their mingling, the latter their separation. Love was therefore the formative principle and hate the destructive. The burning of wood on a hearth proved, in his opinion, the presence of all four elements in that substance. For fire is then evolved from it, along with smoke—which he took to be air: the ash remaining he considered to be earth: and water was deposited on the cold hearth-stone.

Aristotle[1] introduced a fifth element or *quinta essentia*, more subtle and divine than the others, filling celestial space, and out of which the heavenly bodies are formed, while the remaining four elements belong to the earth.

Aristotle was of the opinion that these latter elements were mutually convertible into one other, each having a property in common with that of one of the others. Thus fire is dry and warm; air, warm and moist; water, moist and cold; earth, cold and dry.

But one of these qualities was more dominant in each element than the other. "If the dryness of fire," he said "be conquered by the moistness of water, air [steam] will result: if the heat of air be vanquished by the cold of earth, water will be produced [dew or frost]: if the moistness of water be overpowered by the dryness of fire, earth will result [residue left on evaporating ordinary water]."

The diagram given on p. 4, which is a facsimile from an old alchemical treatise,[2] represents these ideas symbolically.

It is easy to see that many ordinary occurrences lent colour to these views, if indeed they did not originate them. For instance, the production of clouds, and eventually of rain, might appear as the transformation of air into water: while the evaporation of water might readily be taken for the reverse metamorphosis. A lightning flash might be interpreted as the

[1] Born about 384 B.C.
[2] "Pretiosa Margarita Novella," etc. 1656 A.D.

conversion of air into fire, and the solid residue which remains when ordinary water is evaporated to dryness would appear to originate from the water.

It might have been anticipated that when the art of experiment had made some progress, these ideas would have

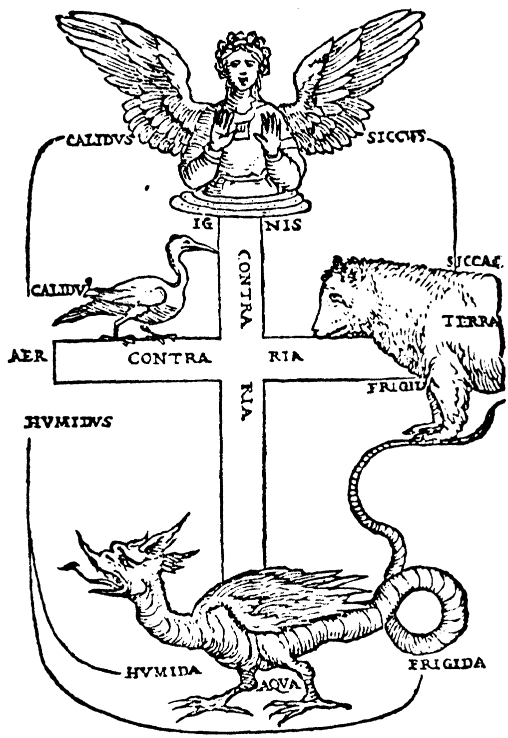


FIG. 1.—Symbolic representation of the four elements.

been quickly dispelled, but such was not the case. Thus Van Helmont, who lived in the sixteenth century, believed with Thales that water was *the* fundamental element, and he brought forward very specious arguments, and what appeared to be very convincing experiments in favour of his opinion, drawn both from the vegetable and animal kingdoms.

For instance, he planted a willow in a weighed quantity

of earth (which was dry when weighed), and during five years supplied it with rain or distilled water only. Weighing the willow both at the time of planting and at the end of the five years, he found that it had increased by 164 lbs., irrespective of the weight of the leaves it had shed.

> "This and several other experiments, which it is needless to state, satisfied him that all vegetable substances are produced from water alone. He takes it for granted that fish live (ultimately at least) on water alone, but they contain almost all the peculiar substances that exist in the animal kingdom. Hence he concludes that animal substances are derived also from pure water." [1]

There can be little, if any doubt, that the Aristotelian philosophy, which throughout the Middle Ages was acknowledged to be the highest expression of scientific truth, gave origin to the fundamental doctrine of alchemy, namely that it is possible to change one metal into another.

For if such prodigious metamorphoses can be accomplished as the conversion of fire into the air, air into water, water into earth, etc., how much more readily ought one metal be capable of passing into an entirely similar substance such as another metal?

The alchemists therefore sought for some medium to effect the conversion of a "base" metal, such as lead or tin, into a "noble" metal, such as silver or gold, and they called this substance the "Philosopher's Stone."

Geber,[2] one of the earliest of the alchemists proper, and one of the most celebrated also, was of the opinion that all metals are composed of two principles, viz., sulphur and mercury; and that the differences in the metals are partly due to the relative proportions of these two principles and partly to the purity or the reverse of the latter. He supposed that the

[1] "Thomson's History of Chemistry."

[2] Yeber-Abou-Moussah-Djafer al Soli (to give him his full title), an Arab of the eighth century.

noble metals contained very pure mercury, and as a consequence that they are unchanged by heat, while the base metals contain so much sulphur that they lose their metallic qualities when calcined.

From the available evidence, it seems probable that the alchemical idea originated in Egypt, but the time of its birth is shrouded in obscurity.

According to Kopp[1] the word "chemia" first occurs in writings of the fifth century.

The following passage is found in the lexicon of Suidas, a Greek writer of the eleventh century:—

"Chemia, the preparation of silver and gold. The books on it were sought out by Diocletian and burnt, on account of the new attempts made by the Egyptians against him. He treated them with cruelty and harshness, as he sought out the books written by the ancients on the chemistry of gold and silver and burnt them. His object was to prevent the Egyptians from becoming rich by the knowledge of this art, lest emboldend by abundance of wealth, they might be induced to resist the Romans."

With the progress of time, and no doubt owing to the discovery of the therapeutic action of some of the metallic salts which were prepared for the first time, such as Glauber's salt (sodium sulphate), the compounds of antimony, etc., chemistry assumed a new direction, to a considerable extent owing to the influence of Paracelsus (a man in other ways of contemptible character), namely, the preparation of and search for chemical medicines, so that we now find alchemy passing into what has been called "Iatro-chemistry."

Robert Boyle[2] altogether combated the Aristotelian and alchemical doctrines regarding the chemical elements, and with him commenced a new era in chemical science.

"In his 'Sceptical Chymist,' he upholds the view that it is not possible, as had been hitherto supposed, to state at once the exact

[1] "Beiträge zur Geschichte der Chemie."
[2] Born at Youghal, in Ireland, in 1627.

number of the elements: that on the contrary, all bodies are to be considered as elements which are themselves not capable of further separation, but which can be obtained from a combined body, and out of which the compound can be prepared. Thus he states, 'that it may be as yet doubted whether or no there be any determinate number of elements; or, if you please, whether or no, all compound bodies do consist of the same number of elementary ingredients or material principles.'"

Boyle, it is clear, was the first to grasp the idea of the distinction between an elementary and a compound body, the latter being a more complicated substance, produced by the union of two or more simple bodies and differing altogether from these in their properties. He also held that chemical combination consists of an approximation of the smallest particles of matter, and that a decomposition takes place when a third body is present, capable of exerting on the particles of the one element a greater attraction than the particles of the other element with which it is combined.

More, however, than for his views on the nature of the elements is science indebted to Boyle, who first felt and taught that chemistry was not to be the handmaid of any art or profession, but that it formed an essential part of the great study of nature, and who showed that from this independent point of view alone could the science attain to vigorous growth. He was, in fact, the first true scientific chemist, and with him we may date a new era for our science when the highest aim of chemical research was acknowledged to be that which it is still upheld to be, viz., the simple advancement of natural knowledge.[1]

The theory of phlogiston is of dual interest in the history of chemistry, for, on the one hand, it has been regarded as the first rational theory introduced into the science, while on the other, the conclusive experiments by Lavoisier, which

[1] Roscoe and Schorlemmer, "Treatise on Chemistry."

finally caused its overthrow, led also to the establishment of one of the most fundamental doctrines in the whole range of physical science, namely that of the conservation or indestructibility of matter.

This theory dealt with the phenomena of combustion, one of the commonest and most striking of all chemical actions.

First propounded by Beccher (1625—1682) and later developed by Stahl (1660—1734) its essence was the assimilation or rejection of a substance which was not exactly fire itself but the matter or principle of fire (*Materia aut principia ignis non ipse ignis*). When a combustible burns, it loses its phlogiston. In order to reproduce the substance, phlogiston must be added to the residue left on combustion. In other words, combustible bodies are compounds. Thus:—

$$\text{Combustible} \rightleftharpoons \text{Calx} + \text{Phlogiston.}$$

There was undoubtedly a certain amount of plausibility in the theory of phlogiston, and it really has a basis of solid truth in it, but for the moment let us glance at some of the experimental evidence brought forward in support of it.

Take this case. Lead when heated smoulders into an ash or calx. Charcoal when burnt leaves a mere trace of ash. Therefore if not phlogiston itself, charcoal is at least very rich in it.

Now heat the calx of lead with charcoal and metallic lead is reproduced.

A fundamental difficulty in the theory of phlogiston soon became manifest. For it was found that the calx of a combustible is heavier than the combustible itself. But people obsessed, so to speak, by a theory are like people afflicted with an incurable disease. The one will not, and the other cannot part with the trouble. The believers in the theory of phlogiston got out of the difficulty just mentioned by supposing that either the metal became more dense, which, in the

opinion of some, would produce an increase in weight, or by the absorption of fiery particles, or again by endowing phlogiston with the property of negative weight.

It sometimes happens that men are, so to speak, born before their time, and that the state of knowledge in their day is not sufficiently advanced for the existing race to be able to appreciate their theories or discoveries. Such was the case with Jean Rey, Hooke, and especially Mayow. All three had studied combustion independently, and the explanation which the first two gave of the phenomenon was partially correct. But Mayow's explanation was correct in all essential particulars.

Hooke had pointed out the similarity of the actions produced by air and by nitre or saltpetre, as regards combustion, and he concluded that the phenomenon is caused by that constituent of the air which is fixed in saltpetre. Mayow developed this theory and clearly showed experimentally that air contains an active and an inactive constituent—the active constituent being what he called *Spiritus Nitro-Aereus*—and that it is absorbed in both combustion and respiration which processes he considered to be analogous. He also distinctly stated that the increase in the weight of a metallic calx is caused by the metal absorbing the *spiritus*, our oxygen, which, however, he failed to isolate.

When Mayow died Stahl was only nineteen, and it is really remarkable that while the former gave in the main the correct explanation of combustion, to which scarcely any attention was paid, the latter gave an incorrect explanation which created a deep impression lasting for nearly a century.

In 1774 Priestley[1] discovered oxygen, but it was reserved for Lavoisier to utilise that discovery (which he unjustly claimed as his own) in the complete overthrow of the phlogiston theory. Lavoisier[2] showed in 1770 that water is

[1] Born 1733.
[2] Born 1743.

not converted into earth when evaporated, a common belief at the time, which he accomplished by the careful use of the balance, an instrument which chemists had much neglected before his time.

"When he became acquainted with the novel and unexpected discoveries of Black (carbonic anhydride), Priestley (oxygen), and Cavendish (composition of water), a new light burst on his mind, and he threw himself instantly with fresh ardour into the study of specially chemical phenomena. He saw at once that the old theory was incapable of explaining the facts of combustion, and by the help of his own experiments, as well as by making use of the experiments of others, he succeeded in finding the correct explanation, destroying for ever the theory of phlogiston, and rendering his name illustrious as having placed the science of chemistry on its true basis."[1]

Lavoisier's investigations regarding the nature of combustion began about 1772, and it would be impossible in a book of this kind to attempt more than a summary of his purely chemical work.

Perhaps the greatest of his services was his insistence on the use of the balance, by which he established (1) the great law of the indestructibility of matter (though it may be doubted if it was fully realised at the time). Then (2) he gave, with abundant experimental proofs, the true explanation of the phenomena of combustion.

It is the oxygen of the air (or active principle) which is operative—sometimes giving invisible products like steam and carbonic anhydride (which would escape detection without special precautions), at others giving visible products like metallic calces and phosphoric anhydride, the oxygen content of which explains the excess of weight over that of the original combustible.

(Here, however, he made a somewhat curious mistake, for

[1] Roscoe and Schorlemmer, "Treatise on Chemistry."

he it was who gave oxygen that name, literally "acid producer," whereas the oxides of metals are as a class *bases*).

In giving the true explanation of combustion, Lavoisier (3) finally overthrew the theory of phlogiston—at least from the material point of view.

Undoubtedly Lavoisier was one of the giants of science, and his output of work in the twenty years during which his labours lasted was prodigious.

But giants have their weaknesses, and Lavoisier's failing was that he largely ignored the work of others and was inclined to take the credit for their discoveries to himself.

Thus he never mentions the theories of Rey, Hooke, and Mayow regarding combustion—so closely approximating his own—though he must have known of them. Again, Priestley told him during a visit he paid to Paris of his discovery of oxygen. He ignored Black's work on carbonic anhydride, and also to a considerable extent Cavendish's classic researches on the composition of water.

If he erred—and there can apparently be no question that he did do so—a terrible fate awaited him, quite unconnected with his scientific career. "For he was accused," during the horrors of the dictatorship of Robespierre in the French Revolution, "along with other farmers general, of defrauding the revenue . . . and on May 8th, 1794, was guillotined at the age of 51."[1]

During practically the whole of the nineteenth century, the ideas of Boyle and Lavoisier were accepted as to the nature of matter, namely, that it is indestructible and uncreatable, and that a certain number of elements or undecomposable bodies exist which by their union with each other give rise to all known substances. The number of these elements increased

[1] Roscoe and Schorlemmer, *loc. cit.*

with the progress of time and discovery, as the following table will show :—

1784. Bergmann : The idea of elements not adopted.
1793. Lavoisier : Mentions 22 elements now recognised as such, together with light and heat; also potash, soda, ammonia, lime, barytes, magnesia, alumina, and silica.
1810. Thomas Thomson : 33 elements now recognised as such, and besides these "muriatic acid" and "nicolanum."
1830. Turner : 54 elements ; also "pluranium."
1850. Graham : 56 elements.
1902. International Atomic Weight table :[1] 76 elements.
1906. " " " " 78 "
1907. " " " " 80 "
1913. " " " " 83 " [2]

The nineteenth century was remarkable for the results of investigations on the second of the two quantities, which together constitute the physical universe, this being energy, while the first is, of course, matter.

Now without giving a detailed history of the views which have been held as to the nature of energy from time to time, a brief general statement may be made.

The idea that heat is a form of matter—a fluid, or at least of the nature of a fluid—was long maintained, and light, electricity, and magnetism were also believed to be of a similar nature.

It is remarkable, however, that Bacon (Lord Verulam) believed heat to be identical with motion (hammering iron until it becomes red hot).

Rumford in 1798 showed that heat is generated by friction.

[1] The numbers of elements given for this and the succeeding years in these tables are those the atomic weights of which have been determined with certainty ; others such as Celtium and the "transient" elements of the radioactive series (see pp. 77, 169—171) with the exception of Niton, are not included.

[2] See p. 41 for this table.

H. Davy in 1799 melted ice by friction with itself, and in 1812 enunciated the proposition:—

"The immediate cause of the phenomenon of heat, then, is motion, and the laws of its communication are precisely the same as the laws of the communication of motion."

But the establishment of the laws or doctrines of the conservation of energy and of its transformations is due to Joule[1] (1840—1843).

In 1840 he published his observations on the heat produced by electric currents under various circumstances, from which he came to the conclusion that there was a relationship between the heat produced and the quantity of zinc consumed in the battery.

Then he measured the amount of work required in a

[1] In the majority, probably, of the great discoveries which have been made, several individuals have taken part, and it is often a matter of controversy as to which of them deserves most of the credit. Such appears to be the case with the doctrine of the conservation of energy.

Thus according to the late Professor Tait ("Recent Advances in Physical Science," 1876), Newton's second interpretation of his third law of motion shows him "to have been in possession of many of the principal facts of the conservation and transformation of energy." And Tait then goes on to say that had Newton known that whenever work is spent against friction the amount of heat produced is proportional to the amount of work producing it, "he would have had no difficulty whatever . . . in passing to the modern statement of the conservation of energy."

Seguin, a nephew of Montgolfier, says that he got from his uncle the idea that heat is certainly not matter, but corresponds with a certain kind of energy; and he also says that he had made various experiments with a steam engine in order to test whether the same quantity of heat reached the condenser as had left the boiler, but he was unfortunately unsuccessful in all his experiments.

Colding, of Copenhagen, a contemporary of Joule, independently came to the conclusion that "Force is imperishable and immortal, and therefore when and wherever force seems to vanish in performing certain mechanical, chemical or other work, the force then merely undergoes a transformation and reappears in a new form, but of the original amount as an active force." According to Tait, Colding began by being metaphysical, and his "metaphysics led him to form certain opinions, but before publishing one of them, he set to work and laboriously brought it to the test of fact. . . . Colding's work is by no means so extensive as Joule's. It is very nearly simultaneous with it, but it is neither so exact nor so extensive."

To J. R. Meyer (1842) is frequently ascribed the merit of the discovery (of the doctrine of the conservation of energy), and especially on the Continent, but his arguments, as well as his claims to priority, and also his experimental methods, have been sharply criticised by his contemporaries Colding and Joule, and also by the late Lord Kelvin and Professor Tait.

magneto-electric machine to generate a given amount of electric current which in its turn may be converted into heat.

Next he directly determined the quantitative relationship between heat and work and expressed it as the "Mechanical Equivalent of Heat."

He also showed that light had a mechanical value.

In fact, by his grand though really simple experiments he conclusively demonstrated that conservation holds for every form of energy, and therefore that all physical phenomena consist in mere transformations of energy, and that a definite quantitative relationship exists between them. Joule therefore to a large extent did the same service for energy as Lavoisier had done for matter.

It may be of interest to give the values of some of these units and their relations to each other:

HEAT.	MECHANICAL ENERGY.			ELECTRICAL ENERGY.		
Calories. (15°C.)	Grm. cms.	Ergs.	Joules.	Volt Coulombs.	Electro-chem. Equivalent of Hydrogen.	Electro-chem. Equivalent (modified).
1·0000 =	$4·272 \times 10^4$ =	$4·1908 \times 10^7$ =	4·1908 =	4·1908 =	0·000433 =	0·0004375
0·2386 =	$1·0194 \times 10^4$ =	$1·000 \times 10^7$ =	1·0000 =	1·0000 =	0·000104 =	0·0001045
23,035 =	$9·841 \times 10^8$ =	$9·654 \times 10^{11}$ =	96540 =	96540 =	1·000	
22,837 =	$9·755 \times 10^8$ =	$9·570 \times 10^{11}$ =	95700 =	95700 =		= 1·000

[Calculation from the most recent electro-chemical equivalent of silver (0·001183) and the accepted Atomic Wt. of Hydrogen (1·008) gives the modified values shown in the seventh column and the bottom row. Recent determinations of the value of the mechanical equivalent of the 20°C calorie have fixed it at $4·185 \times 10^7$ ergs. The 15°C calorie is about 1 part in 1000 greater than the 20°C value.]

The doctrine of the "dissipation" or "degradation" of energy, first enunciated by the late Lord Kelvin, deserves mention, although, as will be shown further on, there are reasons to doubt the ultimate inference which has been drawn from it.

It may be stated somewhat as follows.

Whenever (under ordinary conditions) a transformation of energy takes place, there is a tendency to "run down the scale," that is to say, the quantity being unaltered, the quality becomes deteriorated, or the availability becomes less.

Take the case of heat for example. Its availability depends upon differences of temperature, say between that of the burning fuel on the one hand and that of the condenser on the other, in a steam engine. Suppose now that we have all the heat from a given weight of coal collected in, say, a ton of water at ordinary temperatures; it would be extremely difficult, if not impossible, with any modern appliance to get any work out of it.

> "As long as there are changes going on in Nature, the energy of the universe is getting lower and lower in the scale, and you can see at once what its ultimate form must be, so far at all events as our knowledge yet extends. Its ultimate form must be that of heat so diffused as to give all bodies the same temperature."[1]

Energy and matter, as we have seen, resemble each other in the fact that neither of them can be created nor destroyed, or, in other words, that the universe is endowed, and, so far as our knowledge goes, has always been endowed, with a fixed quantity of each. The different forms of energy can be transformed into each other. Now, is it possible that our so-called elements are also transformable into each other, and that they are merely complexes of some primordial form of matter? If this were established it would greatly simplify our conceptions of the two fundamentals of our universe.

Striking evidence in favour of the view that our elements are compounds of a common constituent will be given in subsequent chapters. Meanwhile this section may be concluded with two observations.

First, the theory of phlogiston had a real and important

[1] Tait, *loc. cit.*

sub-stratum of truth in it, though not in relation to matter. Some pages back the following formula was given as expressing the fundamental idea of the theory of phlogiston :—

$$\text{Combustible} \rightleftarrows \text{Calx} + \text{Phlogiston.}$$

If we substitute energy for phlogiston in that equation, it becomes an absolutely correct expression, thus :—

$$\text{Combustible} \rightleftarrows \text{Calx} + \text{Energy.}$$

This is indeed simply a modification of our present thermo-chemical equations, for example :—

$$\text{Pb} + \text{O} \rightleftarrows \text{PbO} + 50{\cdot}8 \text{ K.}$$

Which may be said to have two interpretations, viz. :—

(1) That when 207 grams of metallic lead (Pb) combine with 16 grams of oxygen (O), energy in the form of heat is evolved, equal to 50·8 larger calories (= 5,080 smaller calories) (see page 14), or

(2) In order to reverse the reaction (that is to obtain 207 grams of lead and 16 grams of oxygen from 223 grams of lead oxide) energy to the same extent must be absorbed.

Second :—

(1) The past few years have seen a revival of the alchemical idea on a sound scientific basis.

(2) A modern view of electricity is that it is of a materialistic nature.

In this way we have some old ideas revived.

CHAPTER II

THE OLDER CHEMISTRY

THE ATOMIC THEORY AND ATOMIC WEIGHTS

THE question whether a piece of anything is capable of only finite or of infinite subdivision must have presented itself to mankind when their intelligence had reached a certain stage of development, and it is interesting to note that the former view was adopted and not the latter; also that this question as to the divisibility of matter formed a subject of speculation more than twenty-three centuries ago.

It has been asserted that the ancient Hindus conceived the idea of atoms or indivisible particles before the Greeks, but the first positive statements regarding this idea, it is usually asserted, originated with the latter, and are to be found in the writings of the two philosophers, Leucippos and Democritos[1] (about 460 B.C.). The former held the view that the world was produced by the falling together of atoms which are the principles of things and are endowed with spontaneous movements of a rotatory nature.

The latter extended this theory, maintaining that the principles of things are not only atoms but include a vacuum also.

Atoms are invisible because of their minuteness, indivisible by reason of their solidity, impenetrable, unalterable and

[1] It should, however, be mentioned that an earlier philosopher of the same nation, Anaxagoras of Klazomenæ (500 B.C.) taught that the primitive constituents of things are small particles which he called *homœomeriæ*, that is *like parts*, and that these were arranged in order out of chaos by an intelligence or *nous*, the chaos consisting of all sorts of particles, while the *nous* sorted them out into similar sets by a centrifugal movement. These ideas probably influenced Leucippos and Democritos in their speculations

infinite in number. They differ from each other in size, shape and weight, are actuated by fate or necessity, and possess an oblique movement in the vacuum causing those of like nature to collide and group themselves together, by which means all things have been formed.

The vacuum is also infinite in magnitude, and is necessary, otherwise the atoms could not move.

While the atomic theory of matter was no doubt not forgotten, it remained in abeyance for many centuries, no doubt for want of any definite evidence in its favour. It is true that certain writers made it a part of their systems during the middle ages, and Descartes adopted it in a modified form.

As at first propounded, it had, however, no experimental basis, nor indeed any positive evidence in its favour, and remained for many centuries merely an hypothesis. Therefore it may be said that when Dalton, early in the last century, came to the conclusion that the quantitative facts relating to the combination of elementary substances like hydrogen and oxygen were associated with the weights of the ultimate particles of those substances or atoms, he did an immense service for chemistry, and laid the foundation stone of at least a century's advance in the subject.

"In all chemical investigations," he says,[1] "it has justly been considered an important object to ascertain the relative weights of the simples which constitute a compound. But unfortunately the inquiry has terminated here; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms might have been inferred—from which their number and weights in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results.

"Now it is one great object of this work to show the import and advantage of ascertaining the relative weights of the

[1] "A New System of Chemical Philosophy," John Dalton, 1808.

ultimate particles both of simple and compound bodies, the number of simple and elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle."

Thus if one particle of water consists of two smaller particles, one being hydrogen and the other oxygen, then as 1 part by weight of the former combines with 8 parts by weight of the latter (or, as Dalton believed, 6·5), their respective atomic weights are as 1 : 8 (or as 1 : 6·5).

The great mistake Dalton made was in laying down arbitrary rules—which were by no means justified—as to the numbers of atoms present in the compound particle, or "molecule," as we now call it.

These rules were as follow :—

1	atom	A + 1	atom	B = 1	atom	C = a	binary	particle.
1	,,	A + 2	,,	B = 1	,,	D = a	ternary	,,
2	,,	A + 1	,,	B = 1	,,	E = a	,,	,,
1	,,	A + 3	,,	B = 1	,,	F = a	quaternary	,,
3	,,	A + 1	,,	B = 1	,,	G = a	,,	,,

"When one compound can be obtained only it must be presumed to be binary.

"When two, they must be presumed to be binary and ternary.

"When three, one we may expect to be binary and two ternary.

"When four combinations are observed we should expect one binary, two ternary, and one quaternary, etc."

"From the application of these rules to the chemical facts already ascertained we deduce the following conclusions :—

"First, water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1 : 7 nearly.

"Second, that ammonia is a binary compound of hydrogen and azote, and that the relative weights of the two atoms are as 1 : 5 nearly.

"In all these cases the weights are expressed in atoms of hydrogen, each of which is denoted by unity." [1]

[1] Dalton, *loc. cit.*

The arbitrariness of these so-called rules was pointed out at the time; nevertheless, one of Dalton's main ideas, as expressed in the words of his quoted above, is still our chief guide to exact atomic weight determinations in all ordinary cases, viz.:—

"From the relative weights in the mass (of the compound) the relative weights of the ultimate particles of the bodies or atoms (*i.e.* of the constituents) might have been inferred."

This we now express by saying that the equivalent of an element is related in an exact arithmetical ratio to its atomic weight.

Just a word as to the exact meaning of the term "equivalent."

Dalton, as we have seen, fixed on hydrogen as the standard of atomic weights; and for some time his example was followed, although hydrogen forms but few compounds, so that but few direct ratios could be observed. On the other hand, oxygen combines with most elements, so that many ratios between the weights of elements and the weights of oxygen in their oxides can be directly determined, and Berzelius referred atomic weights to oxygen = 100.

Two standards were published by the International Atomic Weight Commission up to 1905,[1] viz.:—

$$H = 1. \qquad O = 15{\cdot}88.$$
$$H = 1{\cdot}008. \qquad O = 16.$$

An equivalent may be based on either of these standards and be defined thus:—

(a) The weight of an element combining with, or displacing, 1 part of hydrogen, or 7·94 of oxygen, or (b) the weight of an element combining with 8 parts of oxygen, or combining with or displacing 1·008 of hydrogen.

[1] In the annual table, since published by the Commission, only the second standard (O = 16) is adopted.

The atomic weight is always some exact power of the equivalent. Thus :—

Equivalent of an element = 9. (0 = 16.)

Eqt.		Factor		At. Wt.	Formula of Oxide.
9	×	1	=	9	E_2O.
9	×	2	=	18	EO.
9	×	3	=	27	E_2O_3.
9	×	4	=	36	EO_2.

and so on.

We shall return to the subject of equivalents in relation to exactness of their determination presently.

Meanwhile we may take a general survey of the other methods for determining atomic weights.

Gay-Lussac's Law of Atomic Volumes.—When Gay-Lussac propounded this law he had the advantage of knowing Boyle's Law; he had discovered [1] the law of the behaviour of gases under alterations of temperature, and he was therefore able to realise that in comparing the volumes of different gases they must be measured under similar conditions of temperature and pressure.

In 1805 Gay-Lussac and Humboldt announced that, so far as they could ascertain under such conditions, exactly 2 volumes of hydrogen combine with 1 volume of oxygen. And in 1808 Gay-Lussac made the further discovery that other gases combine in simple volumetric proportions—always provided that temperature and pressure are equal and in addition to this, he also found that the volumes of the products

[1] Dalton in 1802 published six papers in the "Memoirs of the Literary and Scientific Society of Manchester," and in the last of these, according to Thomson, Dalton showed "that all elastic fluids expand the same quantity by the same addition of heat, and this expansion is $\frac{1}{480}$th part for every degree of Fahrenheit's thermometer" (Thomas Thomson: "A History of Chemistry"). The discovery of the law is also attributed to Charles. It is a curious coincidence that as regards most of the laws relating to the physical behaviour of gases, more than one claimant contests the discovery.

of the reacting gases bore a simple relation to those of these latter. Thus he found that:—

2 vols. carbonic oxide	+	1 vol. oxygen	=	2 vols.	carbonic anhydride.
2 ,, nitrogen	+	,, ,,	=	,,	nitrous oxide.
1 vol. ,,	+	,, ,,	=	,,	nitric ,,
3 vols. hydrogen	+	,, nitrogen	=	,,	ammonia.

Also he further observed that the weights of these volumes bore simple relationships to the combining weights of the several gases, and eventually came to the conclusion that *the weights of equal volumes of gases at the same temperature and pressure are proportional to their atomic weights, or, if hydrogen is taken as unity, both as regards the atomic weights and the specific gravities of gases, that the latter are identical with their atomic weights.*

It has been stated[1] that Dalton had also thought of this law, and before Gay-Lussac, but came to the conclusion that it was erroneous, because 1 volume of nitrogen (x atoms) + 1 volume of oxygen (x atoms) give 2 volumes of nitric oxide ($2x$ atoms), instead of 1 volume = 1 atom (or molecule, as we now term it).

In 1811 Avogadro[2] introduced his well-known law, which was a much wider and more comprehensive generalisation than Gay-Lussac's law.

Avogadro's law states that equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules, which he called *molécules integrantes,* and not necessarily the same number of atoms, which he termed *molécules elementaires.*

The weights of these equal volumes are then proportional to molecular weights, but as hydrogen happens to have a diatomic molecule, Gay-Lussac's law is true for all volatile elements having similarly constituted molecules, such as

[1] Ladenburg, "Entwickelungsgeschichte der Chemie," 1869, pp. 62, 63.
[2] *Journ. de Phys., par De la Métherie,* t. 73, Juillet, 1811, pp. 58–76 ; *ibid.,* Februaire, 1814.

oxygen, the halogens, etc. This being the case, it is somewhat remarkable that the atomic weight of oxygen remained 8 until 1843, when it was doubled (along with that of carbon = 6) at Gerhardt's suggestion.[1]

Application of Avogadro's law to the determination of atomic weights.

From the relationship:—

$$\text{Sp. Gr. of gas or vapour} = \frac{\text{Molecular weight}}{2}$$

we can, in a number of cases, ascertain the molecular weights of the individual members of a series of compounds of a given element, and we take as the atomic weight of the element the smallest quantity of it found in any of these molecules. Thus for oxygen:—

Compound.	Specific gravity of vapour × 2 = molecular weight.	Analysis in parts per molecular weight.
Carbon monoxide	28·00	Oxygen = 16, Carbon = 12·00
„ dioxide .	44·00	„ = 32, „ = 12·00
Sulphur „ .	64·07	„ = 32, Sulphur = 32·07
„ trioxide.	80·07	„ = 48, „ = 32·07
Water . .	18·016	„ = 16, Hydrogen = 2·016
Nitric oxide .	30·01	„ = 16, Nitrogen = 14·01

Therefore O = 16.

(This method in exceptional cases may lead to erroneous conclusions. Thus the smallest quantity of aluminum found in the molecules of its inorganic compounds = 54·2, while Al = 27·1.)

Dulong and Petit's Law.—In the year 1819 Dulong and

[1] *Journ. f. Prac. Chem.*, XXVII., p. 439; *Annales d. Chim. et d. Phys.* (3) VII., p. 129; VIII., p. 238.

Petit[1] made careful determinations of the specific heats of the following thirteen elements :—

Bi, Pb, Au, Pt, Sn, Ag, Zn, Fe, Cu, Ni, Co, S, Te,

and found that the products of these specific heats with the corresponding atomic weights was a constant number.

They also pointed out that this was probably a general law, and might be employed in atomic weight determinations.

As the specific heat of a body is the amount of heat required to raise the temperature of unit weight 1° C., the product of specific heat and atomic weight is obviously the quantity of heat required to raise the temperature of an atomic weight of an element 1° C., or in other words Dulong and Petit's law states that all atoms have the same heat capacity.

It has been found that in round numbers this capacity or "atomic heat" is about 6·4,[2] whence it follows that

$$\text{Atomic weight} = \frac{6{\cdot}4}{\text{Specific heat}}.$$

A concrete example will illustrate the use of the method: thus the specific heat of aluminum is 0·214 (Regnault), whence its atomic weight, according to the law in question, is

$$\frac{6{\cdot}4}{0{\cdot}214} = 29{\cdot}9.$$

The equivalent of the metal is 9·033, whence its true atomic weight is

$$9{\cdot}033 \times 3 = 27{\cdot}099 \ (O = 16).$$

It will be seen from this example that Dulong and Petit's law is only an approximation, and indeed it was soon found that the specific heat of an element is often a variable quantity, growing in general with the temperature at which it is determined, and varying with the condition of the

[1] *Annales d. Chim. et. d. Phys.*, X., p. 395.
[2] The figure 6·25 is sometimes given instead.

element, if the latter is capable of existing in more than one modification.

The following are some of the results for carbon[1] :—

Condition.	Temperature °C.	Specific Heat.	Specific Heat × Atomic Weight.
Diamond . .	− 50·5	0·064	0·77
" . .	+ 10·7	0·113	1·36
" . .	+ 206·1	0·273	3·28
" . .	+ 606·7	0·441	5·29
" . .	+ 985·0	0·459	5·51
Graphite. . .	− 50·3	0·114	1·37
" . . .	+ 61·3	0·199	2·39
" . . .	+ 201·6	0·297	3·56
" . . .	+ 977·0	0·467	5·60
Charcoal. . .	0 to + 99·2	0·194	2·33
" . . .	0 to + 233·6	0·239	2·87

The greatest exceptions to Dulong and Petit's law occur among the non-metallic elements, and Nernst[2] gives the following :—

Element.	Specific Heat × Atomic Weight.
Carbon . . .	1·8
Hydrogen . . .	2·3
Boron . . .	2·7
Beryllium . . .	3·7
Silicon . . .	3·8
Oxygen . . .	4·0
Phosphorus . .	5·4
Sulphur . . .	5·4
Germanium . .	5·5

On the other hand, the fewest exceptions to the law are to

[1] Remsen : "Principles of Theoretical Chemistry" (4th edit., p. 73).
[2] W. Nernst : "Theoretical Chemistry." Translated by C. S. Palmer, 1895, p. 154.

be found among the elements with high atomic weights and especially the metals.

The investigations of Neuman (1831), Regnault (1840), and especially of Kopp[1] (1878) led to an extension of the law of specific heats to compounds, and showed that in the latter the different atoms retain their heat capacities, or, in other words, that molecular heat depends on the number of atoms present, thus :—

$$n \times 6{\cdot}4 = \text{molecular heat.}$$

Where n = number of atoms in the compound.

The following examples may be given :—

Substance.	Molecular Heat.	
	Calculated ($n \times 6{\cdot}4$).	Observed.
PbS . . .	12·8	12·7
$PbCl_2$ . . .	19·2	18·5
$CoAs_2$ . . .	19·2	19·2
NaCl . . .	12·8	12·5

Specific heat thus appears to be an "additive property"—that is to say one depending entirely upon the number of atoms present and a function of each, the latter in this case being the same for all metallic atoms.

When all the atoms are not metallic or have a different atomic heat from 6·4, the special values for the atomic heats may be utilised in the calculation. Thus the specific heat of ice is 0·474, and therefore its molecular heat $18 \times 0{\cdot}474 = 8{\cdot}532$. While the molecular heat calculated from the figures given above is

$$2 \times 2{\cdot}3\ (H_2) + 4\ (O) = 8{\cdot}6.$$

Again, the molecular heat of calcium carbonate as determined experimentally is 20·4, while the calculated figure is

$$6{\cdot}4\ (Ca) + 1{\cdot}8\ (C) + 3 \times 4\ (O) = 20{\cdot}2.$$

[1] Liebig's "Annalen." Supplement, Band 3, p. 1, 289 (1864).

From the molecular heat of a compound the heat of a constituent atom may be calculated.

Thus if the atomic heat of lead (6·4) be subtracted from the molecular heat of lead chloride, the remainder corresponds with twice the atomic heat of solid chlorine, thus :—

$$PbCl_2 - Pb = Cl_2. \quad \text{And } \frac{Cl_2}{2} = Cl.$$

$$18{\cdot}5 - 6{\cdot}4 = 12{\cdot}1. \quad \text{And } \frac{12{\cdot}1}{2} = 6{\cdot}05.$$

Similarly

$$NaCl - Na = Cl.$$
$$12{\cdot}8 - 6{\cdot}4 = 6{\cdot}4.$$

And it is thus possible not only to arrive at specific or atomic heats which would be difficult to determine directly, but also to calculate atomic weights. Thus, from the above, the mean specific heat for chlorine is 0·176 and

$$\frac{6{\cdot}4}{0{\cdot}176} = 36{\cdot}3.$$

The Law of Isomorphism (*Mitscherlich*, 1819—1820).—Before considering this law, the following historical particulars may be given.

Hauy[1] regarded crystalline form (*Grundgestalt*) as an important aid in determining the nature of a substance, differences in crystalline form indicating differences in composition, a proposition which Berthollet[2] combated. Gay-Lussac[3] noticed in 1816 that crystals of potash alum grow in a solution of ammonia alum, without changing their form.

Interesting observations were made in this direction by Beudant.[4]

[1] "Traité de Mineralogie."
[2] "Statique Chimique," I. 433.
[3] Kopp: "Geschichte der Chemie," II. 406.
[4] *Annales d. Chim. et d. Phys.*, IV., 72; VII., 399; VIII., 5; XIV., 326.

Gehlen[1] maintained that he had succeeded in obtaining crystals of sodium nitrate in the form of potassium nitrate.

Mitscherlich's discovery of isomorphism originated in an observation which he made, that corresponding salts of phosphoric and arsenic acids crystallised in precisely the same form, and in 1819[2] expressed himself as follows :—

"A similar number of atoms similarly combined produces similar crystalline forms. The similarity in crystalline form is independent of the chemical nature of the atoms and is conditioned only by their number and arrangement."

The law as thus stated is by no means true: thus $BaMn_2O_8$, Na_2SO_4, and Na_2SeO_4 crystallise in the same form, although the first obviously contains a larger number of atoms than the other two. And again, salts of ammonium are isomorphous with the corresponding salts of potassium.

Mitscherlich observed that truly isomorphous bodies are such as crystallise together from the same solution, and at the present time isomorphous substances are generally defined as (1) having a similar composition, (2) crystallising in the same form, and (3) crystallising together from a mixed solution.

In employing this law for the purpose of atomic weight determinations that amount of a given element is taken as its atomic weight which may be regarded as replacing an atomic weight of another element (the atomic weight of which is known) in a given compound without changing the crystalline form of the latter. A couple of examples will illustrate the application of the method.

(1) The equivalent of a certain element is 12·025 and its oxide is isomorphous with cassiterite. Now the latter has the formula SnO_2 and contains four equivalents of tetrad tin or

[1] Schweigger: *Journ. der Chem. u. Phys.*, XV., 383, Anmerk.
[2] *Abhandl. d. Berl. Akad.*, December 9, 1819; *Ann. Chim. et d. Phys.*, XIV., 172.

118 parts by weight united to 32 parts by weight of oxygen; therefore the atomic weight of the element in question (titanium) is:

$$12{\cdot}025 \times 4 = 48{\cdot}1,$$

or crystallised titanic oxide may be considered as resulting from the replacement of an atomic weight of tin by 48·1 parts of titanium.

(2) The correction of the atomic weight of vanadium by Roscoe in 1868[1] is perhaps the most classic example of the services of the method.

Berzelius in 1831[2] had fixed the atomic weight of that element at 68·5, mainly on the grounds:—

(a) That vanadic acid (or as we should now call it vanadic anhydride) is reduced by hydrogen at a red heat, and (b) that the remaining oxide when treated with chlorine at a red heat gives a chloride of vanadium which is volatile and a fixed residue of the original vanadic acid, amounting to exactly one-third of the weight of the vanadic acid originally taken. These changes may be represented as follows:—

Berzelius (O = 8).

(1) $$VO_3 + H_2 = VO + H_2O_2.$$

(2) $$3\ VO + Cl_6 = VO_3 + 2\ VCl_3.$$

Roscoe drew attention first to the fact that vanadinite, which, in addition to vanadium, contains lead, oxygen and chlorine, is isomorphous with pyromorphite, which he formulated as

$$3\ (Pb_3P_2O_8)\ .\ PbCl_2\ ;$$

and with minerals having a similar composition, such as mimetesite $3\ (Pb_3As_2O_8)\ .\ PbCl_2$. and apatite $3\ (Ca_3P_2O_8)\ .\ CaCl_2$. With Berzelius' atomic weight for vanadium this isomorphism was inexplicable.

Roscoe next repeated Berzelius' experiment of reducing

[1] *Phil. Trans.*, 1868, p. 1. Also *Chem. Soc. Journ.*, 1868, p. 322.
[2] *Pogg. Ann. Bd.* XXII., p. 1 (1831).

vanadic acid (at a red heat) in a stream of hydrogen, and to a considerable extent confirmed his quantitative results:—

	Percentage loss.[1]
Berzelius	82·712
Roscoe	82·487

He next contrasted his own views with those of Berzelius (already given) as regards (1) the reduction of vanadic acid at a red heat by hydrogen and (2) the effects of chlorine on the residue thus:—

Roscoe (O = 16).

$$(1)\quad V_2O_5 + 2H_2 = V_2O_3 + 2H_2O$$

$$(2)\quad 3V_2O_3 + 6Cl_2 = V_2O_5 + 4VOCl_3.$$

In support of these views, he showed (a) that vanadic acid (anhydride) must contain more than 3 atoms of oxygen, as it can be formed from an oxide already containing 3 atoms of that element, (b) that the so-called terchloride, which Berzelius supposed was formed when chlorine is passed over the oxide (obtained by the reduction of vanadic acid in hydrogen), is really an oxychloride, and (c) that the vapour density of the latter (86·8 obtained, 88·2 calculated if H = 1) agrees with the formula $VOCl_3$ if V = 51·3. Lastly, with the new atomic weight for vanadium, vanadinite has a similar formula to pyromorphite, namely,

$$3\,(Pb_3V_2O_8)\ .\ PbCl_2,$$

or that it may be considered as resulting from the replacement of 6 atoms of phosphorus in pyromorphite by 6 of vanadium, each of the latter weighing 51·3.

The exact estimation of equivalents is, in the majority of cases, the really important step in determining atomic weights. For, as we have seen, the latter are simple multiples of the equivalents. The factor is not difficult to determine as a rule,

[1] Calculated from the figures given in Roscoe's paper. That Berzelius' figure was slightly too high was due to the presence of traces of phosphorus.

as it is a simple and deduced number, but the equivalent rests entirely on experiments, which are often carried out under difficult and uncertain conditions.

It may be laid down as a general rule that the determination of the equivalent of an element rests on the quantitative analysis or synthesis of compounds, which can be more or less easily obtained in the pure state. The following are some of the chief types of methods:—

(1) *Quantitative analysis, partial, or complete*, but as a rule partial. Example: Heating calcium carbonate to obtain the ratio CO_2 : CaO, whence, knowing the value of C and O, that of Ca can be deduced.

(2) *Direct synthesis.*—Example: The conversion of a weighed quantity of carbon into carbonic anhydride and weighing the latter.

(3) *Indirect synthesis.*—Example: Reducing a weighed quantity of oxide of copper by hydrogen and weighing the resulting water and metallic copper.

(4) *From the densities of elements or compounds in the condition of gases or vapours.*—Example: The density of nitrogen and of certain of its gaseous compounds led not so long ago to a correction of the atomic weight of nitrogen, which has caused a correction in the values of the atomic weights of several other elements.

A more detailed description of the practical details in carrying out one of these methods may next be given.

Hydrogen and oxygen (by methods 3 and 4).—Berzelius and Dulong[1] first made use of this method in 1820, and obtained, as a mean of three experiments:—

Oxygen	88·90
Hydrogen . . .	11·10
	100·00

[1] *Ann. Chim. Phys.*, XV., p. 386.

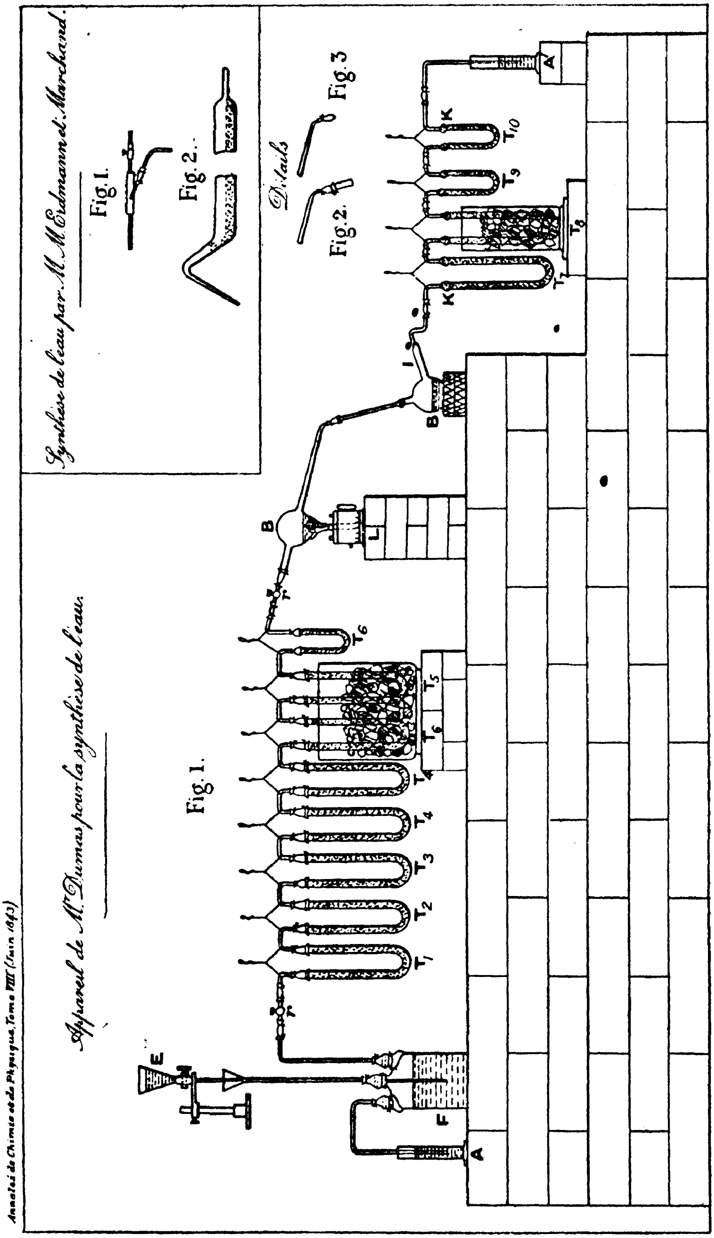

Annales de Chimie et de Physique, Tome VIII (Juin 1843)
Appareil de Mr. Dumas pour la synthèse de l'eau.
Fig. 1.
Synthèse de l'eau par MM. Erdmann et Marchand.
Fig. 1.
Fig. 2.
Détails
Fig. 2.
Fig. 3

FIG. 2.

from which it followed that the equivalent of oxygen was 8·009 (H = 1).

In 1843 Dumas repeated the determination, pointing out the following sources of error in the experiments of Berzelius and Dulong.

(1) Their weighings were not reduced to a vacuum. Some idea of the magnitude of the error thus introduced will be gathered from the fact that Berzelius and Dulong obtained altogether 30·519 grams of water. With the correction for weighing this quantity *in vacuo* the amount would be 30·551 grams, a by no means small correction.

(2) The hydrogen was neither quite pure nor quite dry.

(3) The quantity of water obtained should have been larger if a high degree of accuracy was aimed at.

(4) Certain other corrections.

The apparatus used by Dumas is reproduced as far as possible in reduced *facsimile* from their original paper[1] in the figure shown on p. 32.

The hydrogen was produced by the action of dilute sulphuric acid on zinc, and was purified by passing it through a number of U tubes containing various substances for that purpose, such as lead nitrate, silver sulphate, caustic potash (both in solution and in the solid state), and desiccating agents such as sulphuric acid or phosphoric anhydride. It then passed into the globe containing the heated copper oxide, and finally the water produced was caught in a system of weighed tubes containing first caustic potash and then pumice along with phosphoric anhydride.

The following is a list of the operations performed during an experiment:—

(1) Displacement of the air in the apparatus by hydrogen.
(2) Weighing the vessel containing the copper oxide.
(3) Weighing the water-collecting apparatus.

[1] *Compt. Rend.*, 14, p. 537; *Ann. Chim. Phys.* [3] VIII., p. 189.

(4) Adjustment of apparatus.
(5) Reduction (*i.e.*, heating the copper oxide in hydrogen).
(6) Cooling the apparatus.
(7) Evacuating and weighing vessel containing the reduced copper oxide.
(8) Displacement of the hydrogen by air in the water-collecting apparatus.
(9) Weighing the water-receiving apparatus.

Owing to the length of the operations, the weighings had to be performed at from 2 to 3 A.M., a very unfavourable time, as Dumas remarks, after from nineteen to twenty hours of work.

Dumas obtained more than 1 kilogramme of water in nineteen separate experiments, the mean results being:—

Hydrogen	11·136
Oxygen	88·864
	100·000

whence the equivalent of oxygen worked out to 7·9804 ($H = 1$).

There were still sources of error in the method, *e.g.*, air in the sulphuric acid used; incomplete expulsion of air from such a large apparatus; occlusion of hydrogen by the reduced copper; insufficient drying of the hydrogen; hydrogen passed through strong sulphuric acid becomes slightly contaminated with sulphurous anhydride; the oxide of copper may contain occluded nitrogen or other impurities.

Several other observers utilised the principle of the quantitative synthesis of water for determining the proportions in which hydrogen and oxygen combine, and from the latter the atomic weights of the two elements on the assumption that the formula of water is H_2O, while a number of other workers have derived these atomic weights from the densities of the two gases (method 4).

Data for Re-calculation of Atomic Weight of Oxygen (Clarke).

A. *From Synthesis of Water.*

Date.	Observers.	Ratio.	At. Wt. of H.
1842	Erdmann and Marchand	15·975 ± ·0113	1·00156
,,	Dumas	15·9607 ± ·0070	1·00246
1888	Keiser	15·9514 ± ·0011	1·00305
1870	Thomsen . . .	15·91 ± ·0113	1·00565
1890	Noyes (uncorrected) .	15·8966 ± ·0017	1·00650
1821	Dulong and Berzelius .	15·894 ± ·0570	1·00667
1889	Rayleigh . . .	15·89 ± ·0090	1·00692
1892	Leduc	15·881 ± ·0132	1·00750
1898	Keiser	15·8799 ± ·0046	1·00756
1891—95	Morley	15·8790 ± ·00028	1·00762
1907	Noyes	15·8745 ± ·00021	1·00783
1887	Cooke and Richards .	15·8690 ± ·0020	1·00825
1895	Thomsen . . .	15·8690 ± ·0022	1·00825
1890	Dittmar and Henderson	15·8677 ± ·0046	1·00834
1887	Keiser	15·864 ± ·0150	1·00857
	General Mean. .	15·8779 ± ·00016	1·00769 ± ·00001

B. *From Gaseous Densities.*

Date.	Observers.	Density (H = 1).
1841	Dumas and Boussingault .	15·905 ± ·035
1845	Regnault (corrected) . .	15·9105 ± ·0044
1887	Rayleigh	15·884 ± ·0048
,,	,, ...	15·882 ± ·0023
1889	Cooke	15·890 ± ·0067
1891	Leduc	15·906 ± ·0154
1891—95 ?	Morley (including all data) .	15·8955 ± ·0005
1896	Thomsen	15·8878 ± ·0022
	General Mean . .	15·8948 ± ·00048

A complete list of the final results of the work on both methods, with particulars as to the names of the observers, and the dates of their work, will be found on p. 35.

Meanwhile it should be mentioned that formerly atomic weights were referred to hydrogen as unity; but that now oxygen is universally accepted as the standard with an atomic weight of 16.

Clarke[1] recalculated the results of all the workers on atomic weights, generally adopting the plan of combining similar data together, irrespective of the observers, and finally computing from the general mean so obtained the atomic weight to be established. He says :—

> "Beginning with the ratio between hydrogen and oxygen, each series of experiments was taken by itself, its arithmetical mean was determined and the probable error of that mean was computed. Then the several means were combined, according to the appropriate formula, each one receiving a weight dependent on its probable error. The general mean thus established was taken as the most probable value for the ratio, and at the same time its probable error was mathematically assigned. . . . But although the discussion of atomic weights is ostensibly mathematical, it cannot be purely so. Chemical considerations are necessarily involved at every turn. In assigning weights to mean values, I have been, for the most part, rigidly guided by mathematical rules, but in some cases I have been compelled to reject altogether series of data which were mathematically excellent, but chemically worthless because of constant errors."[2]

If hydrogen and oxygen were perfect gases they would combine in the exact volumetric proportions of 2 : 1. But they are not and they deviate from Boyle's law in opposite directions.

1 "The Constants of Nature," Part V., "A Recalculation of the Atomic Weights" (Smithsonian Miscellaneous Collections), 3rd ed., 1910; 1st ed. 1882; 2nd ed. 1897.

2 For the mathematical part of Clarke's work, see Appendix I. to this chapter.

The exact volumetric ratios have, however, been investigated, with the following results :—

Scott	1 vol. oxygen	= 2·00245 vols. hydrogen	(Lab. Temp.)
,,	,, ,, ,,	= 2·00285 ,, ,,	(Calcd. O.°C.)
Morley	,, ,, ,,	= 2·00274 ,, ,,	(,, ,,)
	Mean value .	2·0028 ± 0·00004.	

"Now including all available data we have a mean value for the density ratio :—

(A) H : O : : 1 : 15·8948,

or, omitting Morley's rejected series,

(B) H : O : : 1 : 15·8991.

"Correcting these by the volume ratio 2·0028 ± 0·00004, the final results from densities become, in terms of the hydrogen unit,

(A) O = 15·8726 ± 0·00058.
(B) O = 15·8769 ± 0·00058.

"Combining these with the result from the synthesis of water and rejecting nothing, we have :—

By synthesis of water	O = 15·8779	± 0·00016
,, gaseous densities	O = 15·8726	± 0·00058
General mean	15·8775	0·00015

"If we reject Keiser's work under the first heading, and omit Morley's defective hydrogen series under the second, we get :—

By synthesis of water	O = 15·8760 ± ·00017 or
	H = 1·00781 ± ·00001
By gaseous densities	O = 15·8769 ± ·00058 or
	H = 1·00775 ± ·000035
General mean	O = 15·8762 ± ·00016 or
	H = 1·00779 ± ·00001."

(Clarke.)

It seems scarcely necessary to observe that the above figures signify that if H = 1, O = 15·8762, or if O = 16, H = 1·00779. The latter figure, as will be seen later, is rounded off to 1·008 in the international table of atomic weights, and is the only

figure on that table which is given to the third place of decimals.

While the correct value of the atomic weight of oxygen is of chief importance, and has been spoken of as the "primary standard" of atomic weights generally, that of silver has in a similar manner been spoken of as the "secondary standard," because it is so intimately associated with the atomic weights of many other elements,[1] notably of chlorine, bromine, iodine, potassium and sodium, while that of nitrogen is also somewhat closely involved.

Stas[2] devoted many years of his life to the determination of the atomic weights of silver and of other elements just mentioned, and his results were for many years regarded as authoritative.

Every possible precaution known at the time was taken by him in relation to:—

(1) Weighings.

(2) Purity of raw materials used originally and of the compounds ultimately obtained.

(3) Methods of analysis or synthesis, etc.

(4) Elimination as far as possible of errors generally.

His work was very extensive and embraced among other determinations that of the percentage of oxygen in various chlorates, bromates and iodates, the ratio of metallic silver to the equivalent weights of several chlorides, bromides and iodides, the ratio in the molecular weights of various salts, and the determination of these molecular weights.

It may be mentioned regarding the first of these sets of determinations that:—

(1) Salts of the type MXO_3 (where X is Cl, Br or I), are readily converted into those of the type MX, whence the ratio

[1] Their haloid salts frequently serving as the starting-out points for the determination of their atomic weights, the halogen content of the former being determined as insoluble silver haloid.

[2] Stas: "Œvres complètes," Brussels, 1894.

$MX : O_3$ can be arrived at, while, the value of the atomic weight of oxygen being known, that of the molecular weight of MX can be easily calculated. In this way Stas arrived at the molecular weights of KCl, KBr, KI, also those of the corresponding Na and Ag salts.

(2) Next the ratio of metallic silver to these nine haloid compounds could be arrived at, and further its ratio to the three halogens themselves.[1]

Up to about 1905 Stas' results for the atomic weights of silver and of the elements more immediately related to it were generally accepted as being practically accurate (except as regards iodine), as will be seen from the following comparison (O = 16):—

	Stas, 1865.	International Table, 1905.
Silver	107·930	107·93
Chlorine	35·457	35·45
Bromine	79·955	79·96
Potassium . . .	39·137	39·15
Sodium	23·043	23·05
Iodine	126·850	126·97
To which may be added Nitrogen . . .	14·045	14·04

Lord Rayleigh, however, in 1894, suspected that Stas' figure for the atomic weight of nitrogen was too high, as he found that its gaseous density[2] agreed more closely with the figures 14·00 than with 14·04. Leduc also (1897) arrived at a similar result in the same way—obtaining the figures 14·01, while Scott (1900) arrived at a similar conclusion by chemical means.

[1] This general plan or scheme of work appears to have been suggested originally by Berzelius.

[2] That is to say, the density of the gas obtained from compounds of nitrogen and therefore argon-free.

It may also be mentioned that Mendeléef, as early as 1890, had pointed out that Stas' value for the atomic weight of iodine was probably too low and that a revision was necessary.

Eventually it seems to have been pretty clearly proved that Stas' figures were vitiated by his having employed too large quantities of materials in his determinations, partly to reduce errors of weighing and partly to diminish experimental errors. In order to avoid the use of excessive quantities of liquids, he carried out his precipitations in too concentrated solutions, which led to "adsorption" or "occlusion" in the precipitates (*i.e.*, of particles of the precipitant), and he even increased this source of error in some of his later determinations by adding his precipitants (*e.g.*, NH_4Cl, NH_4Br, NaCl, NaBr, etc.) in the solid state. Under these circumstances, and especially the latter, occlusion must have occurred in the highest degree, as only undissociated salts are occluded and not their ions.[1]

The following is a brief conspectus of the more modern work which has been done regarding determinations of the atomic weights of silver, etc. :—

DETERMINATION OF CERTAIN ATOMIC WEIGHTS.

Element.	Chief Methods Employed.	Observers.	Date.
Silver	Synthesis of $AgNO_3$.	Richards and Forbes.	1907
Chlorine	,, ,, AgCl.	,, ,, Wells.	1905
Bromine	Determination of Br in various bromides.	,, ,, collaborators.	1890—1908
	Synthesis of AgBr from Ag.	Baxter.	1906
	Conversion ,, into AgCl	,,	,,
Iodine	Conversion of AgI ,,	Ladenburg, Koethner, and Aeuer, Baxter.	1902—1905
	Synthesis ,, ,,	Scott.	1902
	Various ratios, *e.g.*, Ag:I, AgI:AgBr, AgI:AgCl, etc.	Baxter.	1905
Sodium	Conversion of NaCl into AgCl.	Richards and Wells.	,,
	Ratio NaCl:Ag.	,, ,, ,,	,,

[1] Brauner. Abegg's "Handbuch der anorganischen Chemie," Band II., article *Fundamentale Atomgewichte*, which may be usefully consulted for further information.

DETERMINATION OF CERTAIN ATOMIC WEIGHTS—*continued.*

Element.	Chief Methods Employed.	Observers.	Date.
Potassium	As for sodium.	Richards and Staeler.	1907
	Also ratios, KBr:AgBr, KBr:Ag., etc.	„ „ Mueller.	„
Nitrogen	Largely density determinations of nitrogen and gaseous compounds.	Rayleigh, Berthelot, Leduc, Guye and others.	1897—1905
	Also various chemical ratios, *e.g.*, $Ag:AgNO_3$, $NH_4Cl:Ag$, $KNO_3:KCl$, etc.	Scott, Richards and others.	1900—1907

The present table of atomic weights is as follows:—

1913.

INTERNATIONAL ATOMIC WEIGHTS.

		O=16.			O=16.
Aluminium	Al	27·1	Gold	Au	197·2
Antimony	Sb	120·2	Helium	He	3·99
Argon	A	39·88	Holmium	Ho	163·5
Arsensic	As	74·96	Hydrogen	H	1·008
Barium	Ba	137·37	Indium	In	114·8
Bismuth	Bi	208·0	Iodine	I	126·92
Boron	B	11·0	Iridium	Ir	193·1
Bromine	Br	79·92	Iron	Fe	55·84
Cadmium	Cd	112·40	Krypton	Kr	82·92
Cæsium	Cs	132·81	Lanthanum	La	139·0
Calcium	Ca	40·07	Lead	Pb	207·10
Carbon	C	12·00	Lithium	Li	6·94
Cerium	Ce	140·25	Lutecium	Lu	174·0
Chlorine	Cl	35·46	Magnesium	Mg	24·32
Chromium	Cr	52·0	Manganese	Mn	54·93
Cobalt	Co	58·97	Mercury	Hg	200·6
Columbium	Cb	93·5	Molybdenum	Mo	96·0
Copper	Cu	63·57	Neodymium	Nd	144·3
Dysprosium	Dy	162·5	Neon	Ne	20·2
Erbium	Er	167·7	Nickel	Ni	58·68
Europium	Eu	152·0	Niton (Radium emanation)	Nit	222·4
Fluorine	F	19·0	Nitrogen	N	14·01
Gadolinium	Gd	157·3	Osmium	Os	190·9
Gallium	Ga	69·9	Oxygen	O	16·00
Germanium	Ge	72·5	Palladium	Pd	106·7
Glucinum	Gl	9·1			

INTERNATIONAL ATOMIC WEIGHTS—*continued.*

		O=16.			O=16.
Phosphorus	P	31·04	Tellurium...........	Te	127·5
Platinum	Pt	195·2	Terbium	Tb	159·2
Potassium	K	39·10	Thallium	Tl	204·0
Praseodymium ...	Pr	140·6	Thorium	Th	232·4
Radium	Ra	226·4	Thulium	Tm	168·5
Rhodium	Rh	102·9	Tin	Sn	119·0
Rubidium	Rb	85·45	Titanium	Ti	48·1
Ruthenium	Ru	101·7	Tungsten	W	184·0
Samarium	Sa	150·4	Uranium	U	238·5
Scandium	Sc	44·1	Vanadium	V	51·0
Selenium	Se	79·2	Xenon	Xe	130·2
Silicon	Si	28·3	Ytterbium (Neoyt-terbium).........	Yb	172·0
Silver	Ag	107·88	Yttrium	Y	89·0
Sodium	Na	23·00	Zinc	Zn	65·37
Strontium	Sr	87·63	Zirconium	Zr	90·6
Sulphur	S	32·07			
Tantalum	Ta	181·5			

APPENDIX I. TO ATOMIC WEIGHTS.

Clarke gives the following formulæ and explanations regarding the mathematical part of his investigations:—

"The formula for the probable error of an arithmetic mean, familiar to all physicists, is as follows:—

$$(1) \qquad e = 0{\cdot}6745 \sqrt{\frac{S}{n(n-1)}}$$

Here n represents the number of observations or experiments and S the sum of the squares of the variations of the individual results from the mean.

In combining several arithmetical means, representing several series, into one general mean, each receives a weight inversely proportional to the square of its probable error. Let A,B,C, etc. be such means, and a,b,c their probable errors respectively. Then the general mean is determined by the formula

$$(2) \qquad M = \frac{\frac{A}{a^2} + \frac{B}{b^2} + \frac{C}{c^2} \cdots\cdots}{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \cdots\cdots}$$

For the probable error of this general mean we have

(3) $$e = \frac{1}{\sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c} \ldots}}$$

In the calculation of atomic and molecular weights the following formulæ are used. Taking, as before, capital letters to represent known quantities, and small letters for their probable errors respectively, we have for the probable error for the sum or difference of two quantities A and B

(4) $$e = \sqrt{a^2 + b^2}$$

For the product of A multiplied by B the probable error is

(5) $$e = \sqrt{(\mathrm{A}b)^2 + (\mathrm{B}a)^2}$$

For the product of three quantities, A,B,C.

(6) $$e = \sqrt{(\mathrm{BC}a)^2 + (\mathrm{AC}b)^2 + (\mathrm{AB}c)^2}$$

For a quotient $\frac{\mathrm{B}}{\mathrm{A}}$, the probable error becomes

(7) $$e = \frac{\sqrt{\left(\frac{\mathrm{B}a}{\mathrm{A}}\right)^2 + b^2}}{\mathrm{A}}$$

Given a proportion A : B : : C : x, the probable error of the fourth term is as follows :—

(8) $$e = \frac{\sqrt{\left(\frac{\mathrm{BC}a}{\mathrm{A}}\right)^2 + (\mathrm{C}b)^2 + (\mathrm{B}c)^2}}{\mathrm{A}}$$

This formula is used in nearly every atomic weight calculation and is therefore exceptionally important. Rarely a more complicated case arises in a proportion of this kind :—

$$\mathrm{A} : \mathrm{B} : : \mathrm{C} + x : \mathrm{D} + x.$$

In this proportion the unknown quantity occurs in two terms. Its probable error is found by this expression and is commonly large :—

(9) $$e = \sqrt{\frac{(\mathrm{C} - \mathrm{D})^2}{(\mathrm{A} - \mathrm{B})^4} (\mathrm{B}^2 a^2 + \mathrm{A}^2 b^2)} + \frac{\mathrm{B}^2 c^2 + \mathrm{A}^2 d^2}{(\mathrm{A} - \mathrm{B})^2}$$

When several independent values have been calculated for an atomic weight, they are treated like means and combined according to formulæ (2) and (3). Each final result is to be regarded as the general or weighted mean of all trustworthy determinations. This method of combination is not theoretically perfect but it seems to be the one most available in practice."

APPENDIX II. TO ATOMIC WEIGHTS.

Synopsis of some of the chief methods which have been employed for determining the atomic weights of certain of the elements.

ALUMINIUM.—(1) Determination of chlorine in the anhydrous chloride as AgCl (Dumas). (2) Volume of hydrogen displaced by the metal from hydrochloric acid (Terreil) or from caustic soda (Mallet). (3) Weight of alumina on heating ammonia alum (Mallet). (4) Determination of bromine (by titration with silver nitrate) in the bromide (Mallet).

ANTIMONY.—(1) A variety of methods have been employed, which have given results from 118·024 to 121·542 (H = 1). Perhaps the most reliable were those obtained by the following methods: (1) Conversion of the element into Sb_2S_3 (Cooke). (2) Determination of bromine (gravimetrically as AgBr) in $SbBr_3$ and of iodine in the corresponding iodide, by a similar method (Cooke).

ARSENIC.—(1) Determination of chlorine volumetrically in the chloride (Pelouze and Dumas). (2) Determination of bromine in the bromide by a similar method (Wallace). (3) Oxidation of arsenious anhydride to arsenic acid volumetrically by potassium bichromate (Kessler). (4) Conversion of $Na_4As_2O_7$ into NaCl, by heating the former in gaseous HCl (Hibbs).

BARIUM.—(1) Determination of Cl in both the crystalline and in the anhydrous chloride by titration with silver nitrate (Pelouze Marignac, Dumas, Richards). (2) Percentage of water in the crystallised chloride (Marignac). (3) Conversion of the chloride into the sulphate (Turner, Berzelius, Struve, Marignac, Richards). (4) Conversion of the nitrate into the sulphate (Turner). (5) Determination of Br in the bromide both volumetrically and gravimetrically (Richards).

BERYLLIUM.—(1) Conversion of the sulphate into $BaSO_4$ and BeO (by precipitation with barium salt and after removing barium from

the filtrate, precipitating the beryllium with ammonia (Awdejew, Weeren and Klatzo)). (2) Conversion of the double oxalate of ammonium and beryllium into the oxide (Debray). (3) Conversion of the sulphate into the oxide by ignition (Nillson and Petterson, Krüss and Moraht).

Boron.—(1) Determination of water in crystallised borax (Berzelius and Laurent, Hoskyns-Abrahall, Ramsay and Aston). (2) Determination of Br in the bromide (as AgBr) (Hoskyns-Abrahall, Ramsay and Aston). (3) Conversion of anhydrous borax into NaCl, by distillation with hydrochloric acid and methyl alcohol (Ramsay and Aston).

Calcium.—(1) Ignition of calcium carbonate (Berzelius, Erdmann and Marchand, Dumas). (2) Conversion of the oxide into the sulphate (Berzelius). (3) Conversion of the carbonate into the sulphate (Erdmann and Marchand). (4) Determination of Cl in the anhydrous chloride, by titration with silver nitrate (Dumas).

Carbon.—(1) Analyses of organic silver salts by ignition (Liebig and Redtenbacher, Marignac, Hardin, Maumenée). (2) Determination of the weight of carbonic anhydride formed by igniting carbon in oxygen (Erdmann and Marchand, Dumas and Stas, and others). (3) Density of carbonic oxide (Leduc). (4) Conversion of carbonic oxide into carbonic anhydride, by passing the former over a known weight of copper oxide and weighing both the resulting metallic copper and the carbonic anhydride (Stas).

Cobalt and Nickel.—The atomic weights of these are of special interest, as they are almost identical. No less then 16 ratios have worked out for cobalt, and 15 for nickel. The chief methods which have been employed may be summarised thus :—

(1) Analyses of oxalates.
(2) „ „ nickelo-cyanides and cobalti-cyanides.
(3) „ „ sulphates.
(4) „ „ chlorides.
(5) „ „ iodides.
(6) Reduction of oxide (nickel only).
(7) Volume of hydrogen from the metals.
(8) Weight of gold precipitated from a solution of sodio-auric chloride by the metals.
(9) Separation of the metal from nickel carbonyl.

Copper.—(1) Reduction of copper oxide by hydrogen (Berzelius, Erdmann and Marchand, Millon and Commaille). (2) Determination

of both the water and copper (electrolytically) in crystallised copper sulphate (Richards and others). (3) Determination of copper (electrolytically) and bromine (gravimetrically) as AgBr. (4) Electro-chemical equivalent of the metal (Lord Rayleigh, Mrs. Sidgwick, Gray, Shaw, Vanni).

FLUORINE.—Chiefly one general method, namely the conversion of fluorides and especially fluor spar into sulphate (Berzelius, Louyet, Moissan).

GOLD.—Chiefly by determining the metal in various compounds, such as K_2AuCl_5, $N(CH_3)_3HAuCl_4$, $KAuBr_4$ (Berzelius, Krüss, Thorpe and Laurie, Mallet).

IRON.—(1) Oxidation of the metal to Fe_2O_3 (Berzelius, Svanberg and Norlin, Maumenée). (2) Reduction of the same oxide to the metal (Svanberg and Norlin, Erdmann and Marchand, Rivot).

LEAD.—(1) Reduction of lead oxide in hydrogen (Berzelius). (2) Synthesis of the sulphate from the metal (Berzelius, Turner, Stas). (3) Synthesis of the nitrate from the metal (Stas). Synthesis of the chloride from the metal, combined with determinations of chlorine in the chloride (Marignac).

MAGNESIUM.—(1) Estimation of SO_3 in the anhydrous sulphate. (Scheerer). (2) Estimation of MgO in the same salt by ignition (Jacquelin). (3) Ignition of the carbonate (Marchand and Scheerer). (4) Determination of Cl in anhydrous magnesium chloride (by titration with silver nitrate) (Dumas). (5) Synthesis of the oxide (through the nitrate) from the metal (Burton and Vorce).

MANGANESE.—(1) Determination of Cl in the anhydrous chloride by titration with silver nitrate (Berzelius, Arfedson, Turner, Dumas). (2) Reduction of the anhydrous sulphate to sulphide by ignition in a stream of hydrogen (von Hauer, Weeren). (3) Reduction of Mn_3O_4 to MnO by heating in hydrogen and determining the water formed (Rawack). (4) Combustion of manganous oxalate with copper oxide and weighing the carbolic anhydride formed (Schneider). (5) Analyses of silver permanganate (Dewar and Scott). (6) Conversion of manganous oxide into sulphate (Marignac, Weeren).

MERCURY.—(1) Weight of the metal on heating mercuric oxide (Turner, Erdmann and Marchand, Hardin). (2) Ditto on heating mercuric sulphide with copper (Erdmann and Marchand). (3) Ditto from mercuric chloride on heating with lime (Turner, Millon, Svanberg, Hardin). (4) Electrolytic separation of the metal from

various salts, with and without separation of silver in the same circuit (Hardin).

PHOSPHOROUS.—(1) Weight of phosphoric anhydride on burning the element in oxygen (Schrötter). (2) Decomposition of the chloride (tri) by water and titrating the resulting HCl with silver nitrate (Dumas). (3) Weight of silver reduced from a solution of the nitrate by a definite weight of the (vitreous) element (van der Plaats). (4) Analysis of silver phosphate.

SELENIUM.—(1) Reduction of selenious anhydride and selenites to the element (Sacc). (2) Conversion of the element into the tetrachloride and weighing both (Berzelius, Dumas). (3) Weight of silver obtained on igniting silver selenite (Ekman and Pettersson).

SILICON.—(1) Decomposition of the anhydrous chloride by water and titration of the resulting HCl by silver nitrate (Pelouze, Dumas). (2) Decomposition of the anhydrous bromide by water and determination of the resulting SiO_2 (Thorpe and Young).

SULPHUR.—(1) Synthesis of silver sulphide from a known weight of silver (Dumas, Stas, Cooke). (2) Reduction of silver sulphate by heating in hydrogen (Struve, Stas). (3) Conversion of a known weight of silver chloride into the sulphide by heating the former in sulphuretted hydrogen (Berzelius). (4) Conversion of a known weight of sodium carbonate into sulphate (Richards).

TELLURIUM.—The atomic weight of this element is of special interest, on account of its relation to that of iodine and the positions of these two elements in the periodic system. According to the latter, tellurium should lie between antimony and iodine and have an atomic weight less than 126. "Theoretically, Mendeléef assigns it a value Te = 125, but all the best determinations lead to a mean number higher than is admissible under the currently accepted hypotheses. Whether theory or experiment is at fault, remains to be discovered." [1]

(1) Conversion of the element into TeO_2 (by nitric acid). (2) Determination of the Br (as AgBr) in the well crystallised double salt K_2Br_6 (van Hauer, Wills). (3) Determination of the Br (volumetrically with silver nitrate) in $TeBr_4$ (Brauner). (4) Volumetric oxidation of an alkaline solution of TeO_2 by potassium permanganate (Gooch and Howland). Reduction of H_6TeO_6 to

[1] Clarke: "The Constants of Nature," (*loc. cit.*) from which this synopsis has been compiled.

TeO_2 by heating alone and to Te by heating in a stream of hydrogen (Staudenmeyer).

VANADIUM.—(1) Reduction of V_2O_5 to V_2O_3 (Berzelius, Czudnowicz, Roscoe). (2) Determination of Cl in $VOCl_3$ both volumetrically and gravimetrically (Roscoe).

ZINC.—(1) Conversion of the metal into the oxide, either through the nitrate or sulphate (Jacquelain, Axel Erdmann, Morse and Burton). (2) From the volume of hydrogen obtained on dissolving the metal in an acid (Van der Plaats, Reynolds and Ramsay, Mallet). (3) Solution of the metal in a voltameter, and the same current used to precipitate silver or copper (Gladstone and Hibbert). (4) Precipitation of the Br in the anhydrous bromide by silver nitrate (gravimetrically) (Richards and Rogers).

CHAPTER III

THE OLDER CHEMISTRY

THE PERIODIC LAW—PART I.

EARLY in the nineteenth century, Prout suggested that all atomic weights were multiples by whole numbers of H = 1. But this was disproved by the work of several chemists on the atomic weight of chlorine, which was found to lie between 35 and 36. Subsequently the idea was modified by taking one half and then one quarter of the atomic weight of hydrogen as unit.

The chief interest of "Prout's hypothesis," as it has been called, is its association with the probable nature and origin of the chemical elements.

"On the one hand, each of the elementary bodies may represent a separate creation, independent of all the rest and having nothing in common with them. On the other, supposing a relation can be traced between the masses of the atoms of the different elements, then it is open to inquiry whether they may not have a common origin; whether they may not represent several stages in a formative or evolutionary process operating upon a primitive simple material, and whether in that case it may not be possible to transform one into another by the operation of agencies within the range of practical experiment."[1]

It was pointed out by Döbereiner in 1829 (although the idea was not entirely new) that in several families of allied elements three members are closely related. Thus:—

Ca	Sr	Ba
Cl	Br	I
S	Se	Te
Li	Na	K

[1] Tilden: "A Short History of the Progress of Scientific Chemistry."

the atomic weight of the middle term of each being very nearly the arithmetical mean of the atomic weights of the other two. We have in point of fact with the modern data:—

		True At. Wt.
$Sr = \frac{Ca + Ba}{2} = \frac{40{\cdot}07 + 137{\cdot}37}{2}$	$= 88{\cdot}72$	87·63
$Br = \frac{Cl + I}{2} = \frac{35{\cdot}46 + 126{\cdot}92}{2}$	$= 81{\cdot}19$	79·92
$Se = \frac{S + Te}{2} = \frac{32{\cdot}01 + 127{\cdot}5}{2}$	$= 79{\cdot}78$	79·2
$Na = \frac{Li + K}{2} = \frac{6{\cdot}94 + 39{\cdot}10}{2}$	$= 23{\cdot}02$	23·00

And Dumas, in 1858, compared these so-called "Döbereiner's triads" with homologous series, *e.g.*:—

$$CH_3 = \frac{H + C_2H_5}{2} = \frac{1 + 29}{2} = 15$$

$$C_2H_5 = \frac{CH_3 + C_3H_7}{2} = \frac{15 + 43}{2} = 29, \text{ etc.}$$

He also pointed out relations of the kind shown below:—

F = 19	N = 14	F − N = 5
Cl = 35·5 = F + 16·5	P = 31 = N + 17	Cl − P = 4·5
Br = 80 = Cl + 44·5	As = 75 = P + 44	Br − As = 5
I = 127 = Br + 47	Sb = 122 = As + 47	I − Sb = 5

Newlands,[1] in 1864, enunciated the "Law of Octaves," namely, that by arranging the elements in the order of the magnitude of their atomic weights, "the eighth element, starting from a given one, was a sort of repetition of the first, or that elements belonging to the same group stood to each other in a relation similar to that between the extremes of one or more octaves in music."

In the same year he presented a table, "giving a horizontal arrangement of the more important elements, also in the

[1] John A. R. Newlands: "The Periodic Law," 1884.

order of atomic weight with blanks corresponding with some of the missing members of the various groups," and in 1866 he presented the following table:—

	No.		No.		No.		No.		No.		No.		No.		No.
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Ta	46	Tl	53
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb	54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Th	56

Passing over papers by Odling,[1] and a revision of atomic weights which had gradually occurred, we come to 1869 when Mendeléef,[2] in a paper to the Russian Chemical Society, arranged the elements in a tabular form as follows:—

MENDELÉEF'S TABLE OF THE ELEMENTS, 1869.

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104·4	Pt = 197·4
			Fe = 56	Ru = 104·4	Ir = 198
		Ni =	Co = 59	Pd = 106·6	Os = 199
H = 1			Cu = 63·4	Ag = 108	Hg = 200
	Be = 9·4	Mg = 24	Zn = 65·2	Cd = 112	
	B = 11	Al = 27·4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210
	O = 16	S = 32	Se = 79·4	Te = 128?	
	F = 19	Cl = 35·5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85·4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87·6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		? Er = 56	La = 94		
		? Yt = 60	Di = 95		
		? In = 75·6	Th = 118?		

[1] *Quarterly Journ. Science*, Vol. I., p. 642.
[2] "Zeitschr f. Chemie," 1869, p. 405.

MENDELÉEF, 1871.

Series.	Group I. R_2O	Group II. RO	Group III. R_2O_3	Group IV. RH_4 RO_2	Group V. RH_3 R_2O_5	Group VI. RH_2 RO_3	Group VII. RH R_2O_7	Group VIII. RO_4
1	H = 1							
2	Li = 7	Be = 9·4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27·3	Si = 28	P = 31	S = 32	Cl = 35·5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Co = 59 Ni = 59 Cu = 63
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104 Rh = 104 Pd = 106 Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184		Os = 195 Ir = 197 Pt = 198 Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208			
12	—	—	—	Th = 231	—	U = 240	—	— — — —

In this paper he pointed out that the discovery of new elements might be predicted as well as their properties and that certain atomic weights might be corrected.

In the same year, Lothar Meyer contributed an important paper on the same subject[1] in which the principle of periodicity was vindicated in a remarkable manner by the relations of the atomic volumes of the elements to their atomic weights. This table, or rather its present form, will be given presently.

In 1871 Mendeléef[2] again returned to the subject and presented a new table as shown on p. 52.

The present form of the table as it now appears in some of the text-books is shown on p. 54.[3]

We may now examine the law in detail.

The fundamental statement made by Mendeléef was as follows:—

"First the properties of the elements become modified as their atomic weights increase, then they repeat themselves in a new period. The properties of the elements, the constitution of their compounds, as well as the properties of these last, are periodic functions of the atomic weights."

In illustration of this statement, let us examine the elements of the first period, which commences with lithium and, like others of the so-called "short periods," owing to the discovery of the inert elements, consists of eight and not of seven elements.

The properties of these elements and of some of their chief compounds are given in tabular form on p. 55, as well as certain numerical relationships.

The period commences with the well-marked and strongly electro-positive metal, lithium, and next comes beryllium,

[1] Liebig's "Annalen," Supplements VI. and VII., 1870, p. 354.
[2] *Ibid.*, Supplement VIII., 1872, p. 133.
[3] This table is taken from Caven and Lander's "Systematic Inorganic Chemistry," 1906.

The Periodic System.

Increase in oxygenic properties →

GROUPS	O	I A	I B	II A	II B	III A	III B	IV A	IV B	V A	V B	VI A	VI B	VII A	VII B	VIII
SUB GROUPS		A	B	A	B	A	B	A	B	A	B	A	B	A	B	
SERIES 1		H														
,, 2	He	Li		Be		B		C		N		O		F		
,, 3	Ne	Na		Mg		Al		Si		P		S		Cl		
,, 4	Ar	K		Ca		Sc		Ti		V		Cr		Mn		Fe Co Ni
,, 5			Cu		Zn		Ga		Ge		As		Se		Br	
,, 6	Kr	Rb		Sr		Y		Zr		Nb		Mo		–		Ru Rh Pd
,, 7			Ag		Cd		In		Sn		Sb		Te		I	
,, 8	Xe	Cs		Ba		La		Ce (Pr) (Nd) (Sm) (Gd) (Tb) (Er) (Tm) (Yb)				–		–		– – –
,, 9			–		–		–				–		–		–	
,, 10	–	–		–		–				Ta		W		–		Os Ir Pt
,, 11			Au		Hg		Tl		Pb		Bi		–		–	
,, 12	–	–		Ra		–		Th		–		U				

Increase in basigenic properties ↓

Element ...	Li	Gl	B	C	N	O	F	Ne	
Atomic weight (approximate)	7	9	11	12	14	16	19	20	Mean difference 1·9
Character ...	Met.	Met.	Trans.	Trans.	N. Met.	N. Met.	N. Met.	Indft.	
Electric Series	+	+	±	±	—	—	—	0	
Valency ...	I	II	III	IV	V III	IV II	I	0	
Hydride ...	—	—	BH_3 (Indft.)	CH_4 (Indft.)	NH_3 (Base)	OH_2 (Neut)	FH (Acid)	—	
Hydroxide ...	Li(OH)	$Be(OH)_2$	$B(OH)_3$	$C(OH)_4$ $CO(OH)_2$	$NO_2(OH)$	—	—	—	
	(St Base)	(Base)	(B and A)	(Acid)	(Acid)	—	—	—	
Oxide ...	Li_2O	Be_2O_2 (BeO)	B_2O_3	C_2O_4 (CO_2)	N_2O_5	—	—	—	
Chloride ...	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2			

also a metal. Boron may be called a transitional element, for its oxide behaves as an acid towards bases like potash and soda but as a base towards certain acids, *e.g.*, phosphoric acid. Carbon also, though to a less extent, may be regarded as a transitional element, for while in its compounds it behaves as a distinct non-metal, in the free state, as graphite, it conducts electricity, a property characteristic of the metals as a class. Nitrogen, oxygen and fluorine are well marked non-metals.

Regarding the valences of the elements of this period, they increase from the monovalent lithium to the pentavalent nitrogen, but afterwards fall off: thus oxygen is dyad, perhaps in the majority of its compounds, but tetrad in "oxonium" compounds, and fluorine is a monad. As might be expected, the hydroxides of the metals of this period are bases, while those of the non-metals, carbon and nitrogen, are acids. That of boron is, as we have seen, both acid and base.

The next elements in the order of their atomic weights, repeat to a very considerable extent the properties of those of the first period. See p. 57.

The only remarks which seem necessary are, first, as regards valency. The increase up to the pentavalent phosphorus is regular, the latter, like nitrogen, often behaving as a triad. Sulphur in sulphuretted hydrogen is dyad, in sulphine compounds, *e.g.*, $(CH_3)_3SCl$, tetrad, and possibly in sulphuric anhydride, hexad. Chlorine in hydrochloric acid is monovalent, but in perchloric anhydride (which can be obtained) it is heptad. It is possible, therefore, that in this series, or period, the valency steadily increases up to chlorine. But from another point of view, it falls from silicon to chlorine (*e.g.*, in the hydrides).

Secondly, regarding the hydroxides. Up to orthosilicic acid the hydroxides are compounds of the elements with hydroxyl, but from phosphorus to chlorine all are compounds

Element ...	Na	Mg	Al	Si	P	S	Cl	Ar	
Atomic weight (approximate)	23	24	27	28	31	32	35·4	40[1]	Mean difference 2·4
Character ...	Met.	Met.	Trans.	Trans.	N. Met.	N. Met.	N. Met.	Indft.	
Electric series	+	+	±	±	—	—	—	0	
Valency ...	I	II	III	IV	V III	VI ? IV. II	VII ? I	0	
Hydride ...	—	—	—	SiH_4 (Indft.)	PH_3 (F Base)	SH_2 (F Acid)	ClH (S Acid)	— —	
Hydroxide ...	Na(OH) (St Base)	$Mg(OH)_2$ (Base)	$Al(OH)_3$ (B and A)	$Si(OH)_4$ $SiO_2(OH)_2$ (Acid)	— $PO(OH)_3$ (Acid)	— $SO_2(OH)_2$ (Acid)	— $ClO_3(OH)$ (Acid)	— — —	
Oxide ...	Na_2O	Mg_2O_2 (MgO)	Al_2O_3	Si_2O_4 (SiO_2)	P_2O_5	S_2O_6 (SO_3)	Cl_2O_7	—	
Chloride ...	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	SCl_4		—	

[1] Potassium is really next to chlorine in the order of magnitude of atomic weight.

THE LONG PERIODS OF THE PERIODIC LAW.

Group	1	2	3	4	5	6	7	8			9	10	11	12	13	14	15	16
(A)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Dif.	46	47	44	42	42	43	(—)	45	44	47	44	47	45	46	45	48	47	46
(B)	Rb	Sr	Y	Zr	Nb ?	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Dif.	47	50	50	49	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)
(C)	Cs	Ba	La	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dif.	(—)	(—)	(—)	(—)	89	88	(—)	89	89	89	89	87	88	87	86	(—)	(—)	(—)
(D)	—	—	—	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	—
Dif.	(—)	86	(—)	92	(—)	54	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)	(—)
(E)	—	Ra	—	Th	—	U	—?	—?	—?	—?	—?	—?	—?	—?	—?	—?	—?	—?

— signifies missing element.
(—) ,, that difference in atomic weights cannot be directly calculated.

of oxides with hydroxyl, the hydroxyl groups diminishing in number while the number of oxygen atoms attached to the elements increases.

These two periods are in some ways unique, as the simplicity of the arrangement when they are left disappears and complications are then introduced.

Mendeléef called them "Typical Elements"[1] and compared them with the first members of an homologous series of organic compounds.

We now come to an arrangement of the remaining elements in a somewhat zig-zag form—the so-called "long periods," in which the members of alternate series (A and B) more closely resemble each other than do those of consecutive series, *e.g.*, K and Rb as against K and Cu (see tables on pp. 52, 54).

This is perhaps better indicated by spreading the remainder of the table out, see p. 58.

Numerical relationships among the atomic weights.—We have in the *horizontal* rows (periods) as regards the typical elements:—

				Mean difference between consecutive elements.
(1) Li – Ne	= 6·94 to	20·2	= 13·26	= 1·89.
(2) Na – Ar	= 23·00 to	39·88	= 16·88	= 2·41.
1st Long P.—Kr – K	= 39·1 to	82·9	= 43·8	= 2·58.[2]
2nd Long P.—Rb – Xe	= 85·45 to	130·2	= 44·75	= 2·63.[2]

While in the vertical columns (groups) the relations are:—

	(2) Na	Mg	Al	Si	P	S	Cl	Ar
	(1) Li	Gl	B	C	N	O	F	Ne
Dif. in round numbers	16	15	16	16	17	16	16	19·6

[1] Of course, the inert elements had not been discovered at that time.

[2] There should be eighteen elements in this long period, but in point of fact there are only seventeen. The mean is calculated on the former number; also niobium is included in the elements between Xe and Rb, although it is not now on the international atomic weight table, but appears as columbium.

a complication occurs in relation to the differences in the atomic weights (vertical) of the long periods.

With the arrangement

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co
Na	Mg	Al	Si	P	S	Cl		Ar	
16	16	17	20	20	20	20	18 (mean)		

these differences are in rough agreement with those of the two typical periods, but several of the elements are out of their proper position which should be:—

K	Ca	Sc	Ti	As	Se	Br	Kr
Na	Mg	Al	Si	P	S	Cl	Ar
16	16	17	20	44	47	44·5	43

This example illustrates the anomalous position of the typical elements in certain respects, and it may here be remarked that the differences in atomic weights of corresponding members of the long periods varies between 42—50, the average difference in the first two being about 45.

The table on p. 58 shows the long periods and the differences between corresponding members, as well as the calculated differences in cases where one of the corresponding members is missing.

This table does not include the rare earth metals nor niton. It indicates gaps for 38 undiscovered elements, now reduced to 37 by the placing of niton in the space next but one below xenon, as is better seen in the table on p. 62. If uranium finishes the list the number of missing elements is only 25, niton being in the position mentioned.

If manganese is removed to the eighth group,[1] those numbers are reduced by 3; but if the eighth group then contains 4 elements in each period, the total number of elements remaining to be discovered remains as before.

General remarks.—Mendeléef recognised that an eighth

[1] See pp. 58 and 69.

group was necessary, in order to embrace within the periodic system three groups of metals the members of each set of which have very similar atomic weights. These are:—

Fe = 55·8. Ni = 58·7. Co = 59·0.
Ru = 101·7. Rh = 103·0. Pd = 106·7.
Os = 190·9. Ir = 193·1. Pt = 195·2.

It may be remarked that the atomic weight of manganese is 55 (54·93), which more closely approximates that of iron than do either those of nickel or cobalt. Moreover, the compounds of manganese resemble those of iron in many important features, and it will be seen that the position of manganese in the periodic system is practically unique from any point of view.

The question may therefore be asked, would it not be advisable to remove it to the eighth group? This would no doubt disturb the symmetry of that group[1] as it now stands, but, on the other hand, it is conceivable that two new metals[2] remain to be discovered related to ruthenium and osmium respectively, as manganese is to iron.

A certain number of elements, namely those of the so-called rare earths, fail to find places in the above arrangement, and they will be spoken of later. They have a wide range of atomic weights—from about 140 to 176—and therefore come between cerium (140·25) and tantalum (181·5), but their

[1] It should be noted, however, that in Mendeléef's 1871 table the eighth group did in point of fact contain three sets of four metals, copper being added to iron, nickel and cobalt; silver to ruthenium, rodium and palladium; and gold to osmium, iridium and platinum. The same three metals, viz., copper, silver and gold, were also placed by him in the first group, so that they occupied two separate positions in the table.

[2] The discovery of a new element, probably of the platinum group occurring in the dyke rocks in the Nelson district of British Columbia, was announced in 1911 by A. G. French, and was called by him canadium. From his description it appears to be a white metal, soft, and easily melted in the flame of the blowpipe; not readily oxidised, soluble in nitric and hydrochloric acid, also in aqua regia, without residue, and its solution in nitric acid yields no precipitate with sodium chloride. It is found in the metallic condition possibly alloyed with osmium. It occurs in semi-crystalline grains and in short rods, and would appear to be abundant, amounting to from a few pennyweights to 3 ounces per ton of rock.

properties, largely if not entirely, negative their being placed in the blank spaces between these two elements.

Lastly, in connection with this branch of the subject, the following table may be given, in which the inter-relationships of the long periods, the typical elements, as well as of hydrogen and helium to the other elements are given:—

HYDROGEN, HELIUM, TYPICAL ELEMENTS AND LONG PERIODS.

H																	He
Li	Be	B	C											N	O	F	Ne
Na	Mg	Al	Si											P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Yt	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	Nit
—	Ra	—	Th	—	U	—											

We may now consider Lothar Meyer's arrangement, which presents the periodic system in a totally different form, but in one which is equally interesting and important.

It is based on the volumes occupied by atomic weights of the elements (ordinates) plotted against the atomic weights themselves (abscissæ).

The following relationships may be recalled in connection with the table:—

D = Density (mass of unit volume).

$\frac{1}{D}$ = Specific volume (volume of unit mass).

$\frac{\text{At. Wt.}}{D}$ = Atomic volume[1] (volume of the atomic weight or relative volume of the atom).

Regarding the two tables which follow, the first is as far as possible a reduced *facsimile* of the curves constructed by Lothar Meyer and published in the *Annalen* in 1870.

The second has been constructed by the author from data given in the Appendix to this chapter.

[1] It should be mentioned that in order to compare atomic volumes in as absolute a manner as possible, densities should be determined under similar conditions, best at boiling points, but obviously this is impossible in the case of many elements.

Whenever possible, the values for the solid element have been used, but in other cases (as far as possible) the atomic volume of the liquid element at its boiling point has been taken.[1]

It will be seen that there are important points of difference between Lothar Meyer's original curve and the new one which the author has plotted.

This was of course to be expected to a certain extent, for at the time when Lothar Meyer constructed his curve, the inert elements had not been discovered, the atomic weight of uranium was considered by him to be 180 (H = 1), whereas it is now fixed at 238·5 (O = 16), and gases such as hydrogen, oxygen and nitrogen had not been liquefied, so that their true atomic volumes could not be ascertained.

But there are certain anomalies in the new curve to which

[1] It should be mentioned that as early as 1860 Lothar Meyer drew up a table containing most of the elements arranged according to their valences and with the newer atomic weights, which had by that time been introduced, and to quote his own words:—

"At the same time there was shown a regular and continuous change in the valency of the elements from family to family, when the families are arranged in the order of the atomic weights of their members. I . . . also drew attention to the fact that the first differences [*e.g.*, C – Si] with the exception in the case of beryllium, the atomic weight of which was still uncertain, were approximately 16, the two following differences [*e.g.*, As – Sb] approximated to 46, and the last were very nearly double this number, namely 87—90 [*e.g.*, Sb – Bi]."

It is always difficult to decide questions of priority as it so frequently happens that very similar ideas present themselves (as indeed would appear natural in the evolution of any subject) practically simultaneously to several different investigators, and no doubt such was the case with Newlands, Mendeléef and Lothar Meyer as regards the periodic law.

And in this connection, while the complete curve of atomic volumes appears to have been first drawn up and published by Lothar Meyer, Mendeléef tells us that at the Moscow Congress of Russian Naturalists in 1869, he "dwelt upon the relations which existed between density and atomic weights of the elements. The following year Professor Lothar Meyer, in his well-known paper, studied the same subject more in detail, and thus contributed to spread information about the periodic law."

Mendeléef, in the same paper, also drew attention to the services of Carnelly, Laurie, Roberts Austen and others in bringing other properties of the elements, such as those connected with their magnetic qualities, melting points, heats of formation of their haloid derivatives, etc., within the domain of the periodic law. (See the Faraday lecture by Mendeléef in 1889, *Chem. Soc. Journ.* for that year, pp. 634—656; also the Lothar Meyer memorial lecture by Bedson in 1896, *Chem. Soc. Journ.* for that year, pp. 1403—1439.)

attention should be drawn: thus, whereas (as will be seen on comparing the old with the new curve) the former consists of *five* distinct waves,[1] gradually increasing in height with increasing atomic weight, and having alkali metals at their summits in every case, in the latter, there are *six* distinct waves, and indications at least of a seventh,[2] and the first two of these are quite anomalous, as helium and nitrogen are found at their summits, while lithium no longer occupies that position.

But apart from these (and possibly other) anomalies, both sets of curves convey the broad lesson that atomic volumes are to a large extent functions of atomic weights: the position of an element on the curve being closely related to both its physical and chemical properties.

The alkali metals (with the exception of lithium) occupy the crests of at least four waves; also, broadly speaking, electro-negative elements are found on the left (or ascending) parts of

[1] It is true, however, that indications of the commencement of a sixth wave are shown in Lothar Meyer's curve.

[2] Does this point to the existence of another metal of the alkalies of atomic weight 222—226, *i.e.*, between niton and radium? If so, it would almost certainly be radio-active and very possibly a "transient" element.

There are reasons for and against this possibility. On the affirmative side are the facts that niton and radium occupy much the same relative positions on the hypothetical wave as do argon and calcium, krypton and strontium, as well as xenon and barium on the actual waves—at the summits of which are the alkaline metals potassium, rubidium and cæsium respectively.

On the negative side (possibly) are the following differences in atomic weights:—

$$\begin{aligned} Ar - Ca &= 0{\cdot}19. \\ Kr - Sr &= 4{\cdot}73. \\ Xe - Ba &= 7{\cdot}17. \\ Nit - Ra &= 4{\cdot}00. \end{aligned}$$

and also the fact that radium gives origin to niton by a single act or change (see chapters VII. and VIII.). It may also be mentioned that salts of potassium and rubidium possess slight though distinct radio-activity (emitting weak β rays), and it has been stated that the activity of the former varies widely with the source of the salt. On the other hand, salts of the other metals of the alkaline group are not radio-active.

These facts may possibly point to the presence (in potassium and rubidium salts) of a new metal of the alkalies, and, therefore, also may perhaps be used as an argument on the affirmative side of the question under discussion, as again the fact that if the table on p. 62 is consulted two metals are missing in the alkaline series.

the waves, while those of an electro-positive character occur on the right (or descending) parts.

The position of the inert elements is interesting, as coming between the strongly electro-negative halogens and the equally strongly electro-positive metals of the alkalies—just as they do in respect of atomic weights, but (as before pointed out) argon is anomalous in that respect in relation to potassium.

While the metals of the alkalies occupy the summits or crests of the waves, other metals are, as a rule, found in their hollows, and in the case of three of the latter, the metals are those of the eighth group; aluminum, in both the newer and older curve, is found at the base of another wave, but this arrangement (*i.e.*, of metals at the bases of the waves) ceases with elements of lower atomic weight, as boron forms the base of the first wave in both the older and newer curve, while in the latter, oxygen forms the base of the second wave.

It is interesting to notice that certain elements of very similar atomic volumes have often very different properties, *e.g.*, Cl and Ca, Kr and Sr, Xe and Ba, Te and Ce, etc.,

Atomic Volume of Oxygen in oxides.—This may be calculated thus:—

Molecular volume of oxide *minus* volume of atoms other than oxygen in the oxide equals atomic volume of oxygen or of n atoms of oxygen if more than one is present. As examples: —

(1) Molecular volume of $Na_2O = 23{\cdot}7$. Na (At. vol) $= 23{\cdot}6$.

Therefore $23{\cdot}7 - 2(23{\cdot}6) = -23{\cdot}5$. At. vol of O in Na_2O.

(2) Molecular volume of $Al_2O_3 = 25{\cdot}3$. Al (At. vol) $= 10{\cdot}1$.

Therefore $\dfrac{25{\cdot}3 - 2(10{\cdot}1)}{3} = -1{\cdot}7$. At. vol of O in Al_2O_3.

(3) Molecular volume of $SO_3 = 40{\cdot}5$. S (At. vol) $= 15{\cdot}4$.

Therefore $\dfrac{40{\cdot}5 - 15{\cdot}4}{3} = +8{\cdot}4$. At. vol of O in SO_3.

And generally it would appear that the atomic volume of oxygen in :—

(1) Strongly basic oxides is *negative.*

(2) Oxides of the transitional elements is nearly zero.

(3) Strongly acid oxides is *positive.*

Mendeléef[1] gives the following for the oxides of two short periods :—

	S	V	Δ		S	V	Δ
Na_2O ...	2·6	24	− 22	K_2O	2·7	35	− 55
Mg_2O_2 ...	3·6	22	− 3	Ca_2O_2 ...	3·15	36	− 7
Al_2O_3 ...	4·0	26	+ 1·3	Sc_2O_3 ...	3·86	35	0
Si_2O_4 ...	2·65	45	+ 5·2	Ti_2O_4 ...	4·2	38	+ 5
P_2O_5......	2·39	59	+ 6·2	V_2O_5......	3·49	52	+ 6·7
S_2O_6......	1·96	82	+ 8·7	Cr_2O_6 ..	2·74	73	+ 9·5

In which :—

S = Density.

V = Specific volume.

Δ = Difference between volume of the oxygen compound and that of the parent element divided by the number of oxygen atoms in the compound.

"Δ thus representing the average increase of volume for each atom of oxygen contained in the salt forming oxide."

Melting points vary periodically, e.g. :—

(1) Elements at, or immediately preceding, *minima* in atomic volume have high melting points, thus B,C,Si. Also group 8 (long periods). Ti, Mo, Cr., etc. (It will be seen that in the new curve oxygen is anomalous in this respect.)

(2) Those following minima on ascending curve have low melting points. Thus P, S, Cl; Ga, As, Br; Cd, Sn, I, Hg, Tl, Pb, etc.

In general only those elements are readily fusible and

[1] Faraday Lecture, *Chem. Soc. Journ.* 1899, pp. 634—656.

volatile, the atomic volumes of which are greater than those of the elements immediately preceding them in atomic weight or on the ascending parts of the curve.

Richards[1] in his address to the Chemical Society in 1911, drew attention to the possibility of atoms being compressible, an idea which, as he remarks, though not necessarily dependent on the belief that atoms are built up of much smaller particles, is strictly consistent with it.

He then described a special form of apparatus which he had devised for ascertaining the compressibility of elementary substances and the results which he obtained with it in a certain number of cases. He showed that these closely followed Lothar Meyer's curves of atomic volumes and said :—

"The parallelism cannot but suggest that atomic volume and compressibility are fundamentally connected: and indeed the theory of compressible atoms gives a plausible explanation of the connection. We should expect the large atomic volumes to be more compressible, because we might infer from their bulk that they are not under as great pressures as the small volumes, and material under slight pressure is likely to be more compressible.

"Moreover, the bulky and easily compressible elements are in most cases more easily melted and volatilised than those possessing small volume and slight compressibility. That is just what we might expect: all these properties combine to indicate that the bulky elements have less cohesion than the compact ones."

Richards, in the same paper, shows that on plotting the heats of formation of certain compounds of the elements, such as the chlorides and oxides, against the atomic weights of the same elements, interesting relationships are apparent. In doing this, the heat of formation is taken as the gram equivalent of

[1] "The Fundamental Properties of the Elements" (Faraday Lecture, *Chem. Soc. Journ.* 1911, pp. 1201—1218).

oxygen or chlorine, the compounds being those of a typical kind, such as ECl, ECl_2, ECl_3, etc.

His results are suggestive and his diagram is reproduced in *facsimile* below.

Many other physical properties, such as malleability, coefficient of expansion by heat, atomic refraction, colour of

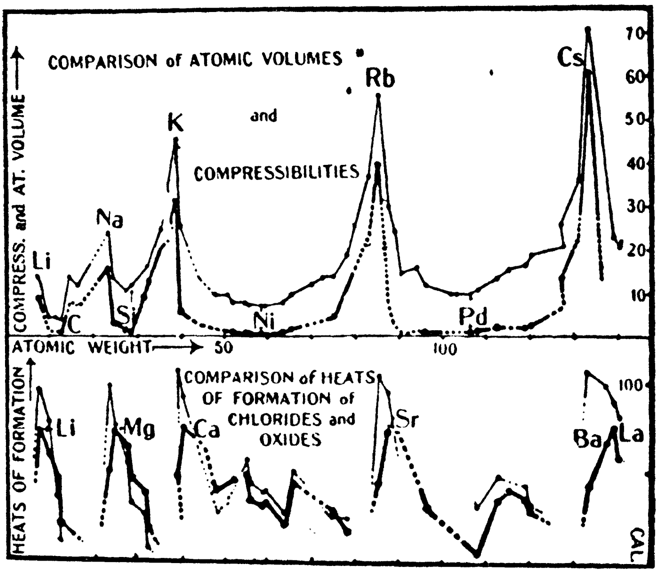


FIG. 5.

salts, conductivity for heat and electricity, etc., also appear to be related to atomic volumes.

To sum up, as regards the periodic law as presented by Mendeléef.

The elements are arranged in tabular form in horizontal rows, each horizontal row constituting a "period" in which, with increasing atomic weight, the properties of the elements become modified—those with low atomic weights being (broadly speaking) metallic in properties, while those of higher atomic weights are of non-metallic character.

In a new period we have to a large extent a repetition of the preceding one, and therefore analogous elements appear in the same vertical columns or "groups."

The first two periods are of a special nature, and the elements in them are spoken of as "typical." After these, the members of the alternate periods more closely resemble each other than do those of the consecutive periods.

If spread out, the elements in two of the latter amount to eighteen.

One of the features of this arrangement is the somewhat remarkable fact that three series (each of three elements) are grouped together in the eighth group. Another feature is that this arrangement is not symmetrical, as seven elements precede this group, while eight follow.

If, however, the inert elements are placed at the commencement of the groups, in accordance with the order of valences (as is done in the table in Caven and Landor's book), and manganese is added to the eighth group, the table becomes symmetrical; thus with the first long period:—

$\overbrace{\text{Ar K Ca Sc Ti V Cr}}$ $\overbrace{\text{Mn, Fe, Ni, Co}}$ $\overbrace{\text{Cu Zn Ga Ge As Se Br}}$

Regarding the groups, even if the arrangement of long periods is adopted, the basigenic properties of the elements increase with atomic weight. (Compare Be with Ba, C with Th, N with Bi, O with Te, etc.)

While as regards the periods, if the short arrangement is adopted, both the valency and acidic properties increase, as before stated, with rising atomic weights; while with the long period arrangement there is a waxing up to the seventh term in both respects, and after the eighth group is passed, this may be said to be again repeated.

In addition to the analogies found among elements of the same groups, others often of an equally striking kind are

sometimes found among those of neighbouring groups in the same or following period, or in other words, elements of different valences often closely resemble each other. A few cases of the kind may be examined.

Beryllium and Aluminum (Groups II. and III., Table, p. 54).—Both elements occur together (Beryl and Chrysoberyl). Both are silver-white and light metals, not very easily reduced from their compounds and of medium melting points.

Both are soluble in hydrochloric and sulphuric acid, also in alkalies, but are scarcely soluble in nitric acid.

Each forms a soluble deliquescent chloride, and each a gelatinous hydroxide soluble in alkalies.[1]

Each forms a single oxide which, when dry, is a white powder. Both metals readily form basic salts.

Boron and Silicon (Groups III. and IV.).—Both of these elements are hard to reduce and fuse only at high temperatures.

Both occur in nature as oxides, either alone or combined with those of metals, and these oxides when obtained artificially are, when dry, white and amorphous.

Their compounds with hydrogen are gases which show neither basic nor acidic properties.

Their hydroxides are (at ordinary temperatures) only faintly acidic and readily lose water.

Each forms a single chloride which is a volatile fuming liquid and at once decomposed by water into hydrochloric acid and the hydrate.

Their fluorides are gases which also yield the hydroxides on contact with water together with acids, namely :—

$$HF, BF_3 = HBF_4.$$
$$2HF, SiF_4 = H_2SiF_6.$$

[1] Beryllium hydroxide is also soluble in ammonium carbonate, while aluminum hydroxide is insoluble, properties which are taken advantage of in separating the two from each other.

	Nitrogen.	Phosphorus.	Sulphur.
Condition	Gas	Solid	Solid
Colour	Colourless	Almost colourless to red	Yellow
Allotropic modifications	Two [1]	Several	Several
Molecule	N_2	$P_4 — P_2$	$S_8 — S_2$
Atomic volume at boiling point ...	30·8 (at critical temp.)	20·91	21·60
,, heat	6·4	5·4	5·4
Tendency to oxidise (at relatively low temperatures)	None	Very considerable	Marked
When ignited (in oxygen)	No effect [2]	Burns to P_2O_5	Burns to SO_2 and SO_3
Hydride (chief)	NH_3 (strong base)	PH_3 (weak base)	SH_2 (faint acid)
Affinity for halogens	Very slight	Very considerable	Well marked
Organic compounds	$R\,NH_2$, R_2NH, R_3N } (Bases)	$R\,PH_2$, R_2PH, R_3P } (Bases)	RSH (Faint acid), R_2S (Faint base ?)
	R_4NX	R_4PX	R_3SX
Oxidation of organic compounds (direct)	—	$RPO\,(OH)_2$	$RSO_2\,(OH)$
	—	$R_2PO\,(OH)$	—
	—	R_3PO	R_2SO
	—		R_2SO_2

[1] An allotropic modification of nitrogen was obtained by Strutt by submitting pure nitrogen in an exhausted tube to the action of the discharge from a Leyden jar (*Proc. Roy. Soc.* 1911. 85, App. 219—229).

[2] Except at very high temperatures.

Phosphorus and Sulphur (Groups V. and VI.).—The remarkable analogies between these elements was first drawn attention to by Crum-Brown and Letts,[1] who also pointed out that in many respects sulphur more closely resembles phosphorus than the latter resembles its group neighbour, nitrogen. This will be seen from the Table on p. 71.

Thallium and Lead (Groups III. and IV.).—Both metals are easily reduced and resemble each other very closely in physical properties, such as colour, softness, relatively low melting-point, etc. In chemical properties, many of the thallous compounds resemble those of lead; thus the chlorides of both are colourless, sparingly soluble in cold water, but much more soluble in boiling water, from which they separate in the crystalline form on cooling. The iodides of both are yellow and sparingly soluble.

Doubtful Atomic Weights and the Periodic Law.—As each element has a definite place in the periodic system, it is justifiable in certain cases to assign a particular atomic weight to an element, from considerations based on the law which would be doubtful otherwise, and in this way certain atomic weights have been corrected. One or two examples may be given.

Beryllium.—Old equivalent 6·9. Equivalent in 1871, 4·7. Equivalent at the present time 4·55.

The following are some of the possible atomic weights with the corresponding formulæ of the oxide :—

Atomic Weight.	Formula of Oxide.
4·55	Be_2O
9·10	BeO
13·65	Be_2O_3
18·80	BeO_2
etc.	etc.

[1] *Trans. Roy. Soc. Edinburgh*, XXVIII. p. 571, 1878, and Letts. *ibid.* XXX., p. 285, 1880.

The following were Mendeléef's arguments for assigning its present position to the element and the consequent atomic weight 9·1 (9·4 when he made the change).

Be = 4·7. No element (apart from hydrogen) is known with such a low atomic weight, and if that were the atomic weight of the element, it would in all probability have very remarkable properties.[1] It would no doubt be intermediate between the alkali metals and hydrogen, as it would be monatomic.

Be = 14·1.[2] The element could find no place in the periodic system. Supposing that it could do so, it would have to form very acid oxides, such as BeO_3 or Be_2O_5, and easily give a compound with hydrogen of a basic character, and it would be a non-metal.

Be = 18·8. It must then resemble fluorine and be a gas. It would give no oxide and would be a non-metal. Its hydrogen compound would be a strong acid.

Beryllium is a silver-white and light metal (sp. gr. about 2), thus resembling both magnesium and aluminum, as it does in many of its compounds.

Heated, it burns brightly, forming a white amorphous oxide (Mg), while its hydroxide strongly recalls that of aluminum (*e.g.*, solubility in alkalies). Its deliquescent chloride, and the readiness with which that body combines with other chlorides, resembles in those respects the chlorides of both aluminum and magnesium. Its sulphate easily crystallises and effloresces like magnesium sulphate, and its carbonate and phosphate are insoluble, just as are the corresponding magnesium compounds.

In short, with Be = 9·4 (really 9·1), the element enters the system and all the above-named properties harmonise with the position it then occupies.

[1] Helium, since discovered, has nearly this atomic weight, and has, in point of fact, remarkable properties.

[2] This was the atomic weight formerly assigned to it.

Indium.—Equivalent 38·33. If the oxide be InO (as was formerly thought), In = 76·66. Then it would have to be placed between arsenic and selenium, where there is no room for it. If the oxide be In_2O_3 (In = 114·99) (really 115·0 in round numbers), the element finds a position between cadmium and tin and below gallium. This change, which was suggested by Lothar Meyer, was supported by Bunsen's determination of the specific heat of the metal, which he found to be 0·0057, from which:—

$$\text{Atomic weight} = \frac{6{\cdot}4}{0{\cdot}057} = 112{\cdot}5.$$

The other properties of both indium and of its compounds are in harmony with the position required by the atomic weight 115·0 approximately.

Uranium.—Formerly the atomic weights 60, 120 and 180 [1] were assigned to this element at different times, but with the former it would have to be placed between nickel and copper, and with the second between antimony and tellurium. With atomic weight 240,[2] Mendeléef showed that the element falls into group VI. (Table, p. 52), and becomes the heaviest analogue of chromium and the element of highest atomic weight yet known. This place fits it well, thus the highest oxide UO_3 is acidic, but less strongly so than CrO_3.[3] Further the highest chloride resembles $MoCl_4$ in volatility. Determinations of the vapour density of the chloride and bromide by Zimmermann confirmed Mendeléef's views as to the position of this element in the periodic system.

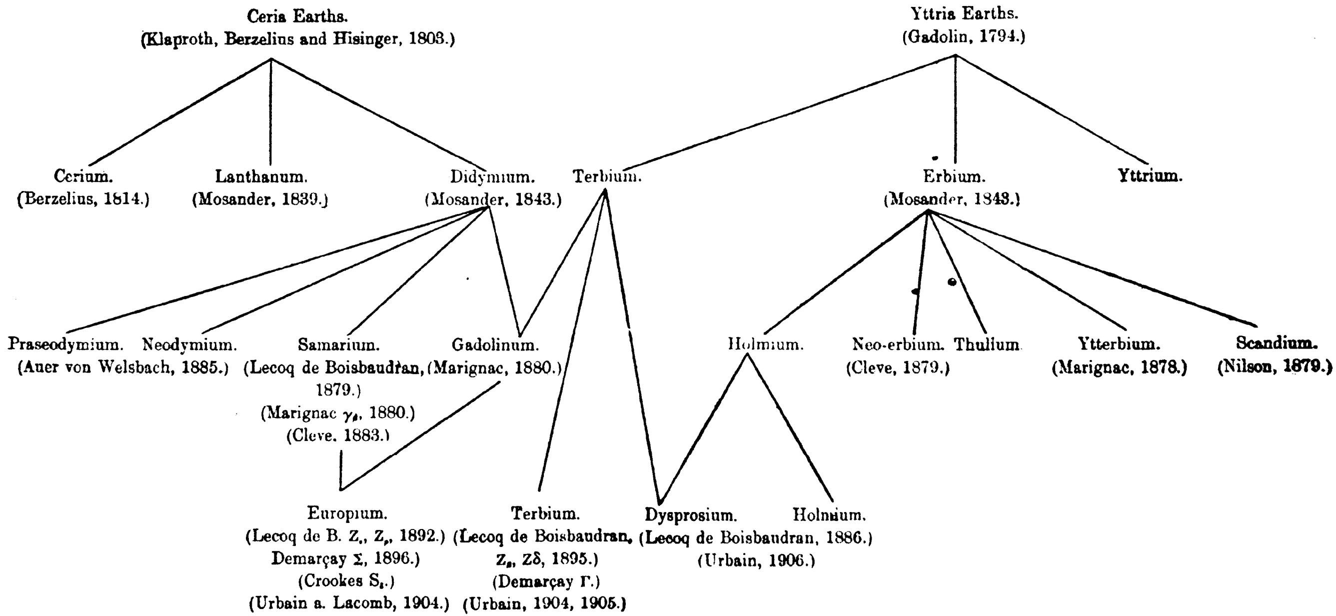
Elements of the rare earths and their position in the periodic system.—Gadolin, in 1704, discovered a new earth (later named Gadolinite in his honour) which was called

[1] See Lothar Meyer's atomic volume curve, p. 62.

[2] Now 238·5 (O = 16).

[3] It has been already remarked that the groups are descended, the metallicity of the elements increases, and, as a consequence, the basicity of the oxides increases also.

HISTORICAL SCHEME REGARDING THE DISCOVERIES OF RARE EARTHS.



The elements are so arranged that expression is given to their inter-connections and the degree of their relationships, as shown by the order of their separation on fractionating.

yttria, and in 1803 Klaproth, on the one hand, with Berzelius and Hisinger on the other, discovered in cerite (another Swedish mineral) a second new earth to which the name ceria was given.

Later, other minerals, such as samarskite, euxinite, fergusonite, xenotime, etc., containing these as well as other earths, were discovered, partly in Scandinavia and Greenland, also in the Ural mountains, Australia and America; while the invention of the incandescent gas mantle by Auer von Welsbach, about 1884, created a commercial demand for thoria, as well as for certain of the rare earths in question, which is at present supplied almost entirely by monazite, or rather monazite sand, which occurs in certain rivers and on the sea coast on the American continent, especially in Brazil, as well as North and South Carolina.

The complete separation from each other of the different earths of this group has proved be be both difficult and tedious, as will be seen from the number of operations necessary in the case of lutecium. In fact the investigation of the rare earths has extended over a century and is probably still incomplete. It may also be mentioned that comparatively few of the metals of these earths have as yet been isolated.

The scheme on p. 75 is taken from Abegg's book.[1]

It does not include the two metals, lutecium and celtium, more recently discovered by Urbain, in 1907 and 1911 respectively.

The first of these (lutecium) was originally obtained by him from 50 grams of ytterbia by fractional crystallisation of the nitrates of the rare earths which it contains; later, from the earths obtained from xenotime, by first separating a number of the allied earths as ethyl-sulphates; conversion of the

[1] "Handbuch der anorganischen Chemie." Dritte Band. Erste Abtheilung. Article by R. J. Meyer ("Seltene Erde"), p. 140.

mother liquors from these into nitrates and the fractional crystallisation of these nitrates. No less than 15,000 separate crystallisations were necessary.

The second (celtium) was discovered in the mother liquors of the nitrates obtained in the isolation of lutecium from gadolinite earths. The oxide of the new element is characterised by a magnetic susceptibility three or four times less than that of lutecia. The arc spectrum shows a number of lines, of which five are specially intense. The chloride is somewhat more volatile than that of lutecium, but less so than that of scandium. The hydroxide is less basic than that of lutecium, but more so than that of scandium.

As a class, the rare earths are basic oxides. The elements of the series have been divided into three groups as follows:—

Cerium group.	At. Wt.	Terbium group.	At. Wt.	Ytterbium group.	At. Wt.
Scandium	44·1	Europium	152·0	Dysprosium	162·5
Yttrium	89·0	Gadolinium	157·3	Holmium	163·5
Lanthanum	139·0	Terbium	159·2	Erbium	167·7
Cerium	140·25			Thulium	168·5
Praseodymium	140·6			Ytterbium (Neo-ytterbium)	172·0
Neodymium	144·3			Lutecium	174·0
Samarium	150·4			Celtium	176·0

(On reference to the international table of atomic weights, it will be seen that celtium is not included in the list of elements, while holmium was only placed in the table for 1913.)

In perhaps the majority of cases the separation of these elements from each other is attended with great difficulty owing to the close similarity of their compounds, but the above classification is based upon the differences in solubility of the double sulphates of the elements and potassium sulphate, the cerium group giving practically insoluble double salts, the ytterbium group giving such as are readily soluble,

while the solubility of these double salts in the case of the terbium group is intermediate between the two.

Further separation is effected by some process of fractionation, such as partial precipitation with ammonia, fractional crystallisation of nitrates, formates, ethyl-sulphates, oxalates, etc., or by taking advantage of the fact that the nitrates are decomposed into oxides at different temperatures.

Regarding the position of these elements in the periodic system, it will be seen that scandium, lanthanum, and cerium fall into definite positions, but such is not the case with the others, and various suggestions have been made on this point of which two may be mentioned, namely:—

(1) To interpolate them in one group (IV.) between cerium (atomic weight 140) and tantalum (atomic weight 181) as is done in the Table on p. 54.

(2) To expand the table into three dimensions of space, cerium, and the elements following it up to lutecium lying on a plane at right angles to that of the other elements.

But it is difficult to see what intelligible meaning attaches itself to either of these suggested arrangements.

Regarding atomic volumes, only three of the elements appear to have been isolated. These are:—

	At. Wt.	At. Vol.
Praseodymium	140·6	20·765
Neodymium	144·3	21·709
Samarium	150·0	19·3

The atomic volumes of these three approximate each other therefore pretty closely.

Finally, as regards this part of the subject, mention may be made of Crookes' experiments on salts of certain of the rare earths which, largely on spectroscopic evidence, he considered he had separated into several different constituents. This led him, in his Presidential Address to the Chemical

Society in 1888, to express the view that certain of the rare earth elements (if not most) were what he termed "meta-elements," a class of bodies which he apparently regarded as not exactly differing atomically, but differentiated by the aggregation of their atoms to molecules of different structures and of different sizes.

His views have, however, been strongly combated by Lecoq de Boisbaudran, Marignac and others, who explained his spectroscopic results as being due to the presence in the salts which he examined of minute traces of foreign bodies, and later observations appear on the whole to have confirmed that view.

Appendix to Periodic Law, Part I.

Data from which the author's curve of atomic volumes was constructed. (The elements are arranged in the order of magnitude of their atomic weights.)

Element.	Atomic Vol.	Density. L = Liquid. In other cases solid.	Authority for Density.
Hydrogen ...	14·4	0·07 (L)	Moissan, "*Traité de Chim. Minérale.*"
Helium	26·6	0·15 (L)	Ohnes, *Chem. Soc. Journ.*, 1908, Ab. II., p. 944.
Lithium	11·7	0·5936	Bunsen and Matthieson.
Beryllium ...	4·9	1·85 (20)·	Humpidge, *Proc. Roy. Soc.*, 1886.
Boron	4·5	2·45	Moissan, *Ann. Chem. Phys.*, 1895.
Carbon, Diamd.	3·7	3·25 (mean)	" "*Traité de Chim. Minérale.*"
Carbon, Graph.	5·5	2·2	" " " " "
Carbon, Charl.	7·6	1·58 (mean)	Abegg, "*Handbuch, d. anorg. Chem.*"
Nitrogen ...	30·8	0·455 (L at crit. temp.)	Wroblewski, *Compt. rend.*, 102.
Oxygen	13·3	1·2 (L)	Mean results; Olzewski, Liveing, Dewar, etc.
Fluorine ...	16·7	1·14 (L)	Moissan and Dewar, *Compt. rend.* 124 and 125.
Neon	20·2 ?	1·0 ? (L)	Ramsay and Travers, *Trans. Roy. Soc.* 197, p. 88.
Sodium	23·7	0·9725	Hagen, *Wied. Ann.* 19.
Magnesium ...	13·9	1·75	Deville and Caron, *Compt. rend.* 44.
Aluminum ...	10·4	2·6	Mean of various observers.
Silicon	11·7	2·42	Mean (Amorph), Vigouroux, *Annales*, 1897; (Cryst) Harmenung, *Pogg. Ann.*
Phosphorus ...	15·5	2·0	Mean (Vit.) Various; (Red) Hittorf.

Element.	Atomic Vol.	Density. L = Liquid. In other cases Solid.	Authority for Density.
Sulphur	15·8	2·03	Mean of various modifications and observers.
Chlorine ...	23·5	1·5071 (L)	Drugman and Ramsay, *Journ. Chem. Soc.*, 1862.
Argon	32·9	1·212	Ramsay and Travers, *Trans. Roy. Soc.*, 1900.
Potassium ...	44·7	0·875	Baumhauer, *Berichte*, 6, 1875.
Calcium	23·6	1·70	Mean, Moissan, *Traité de Chim. Minérale.*
Scandium ...	?	?	
Titanium ...	9·9	4·87	Moissan, *Traité de Chim. Minérale.*
Vanadium ...	9·3	5·5	Roscoe.
Chromium ...	8·9	5·8	Moissan, *Traité de Chim. Minérale.*
Manganese ...	7·4	7·43	Mean of various, Moissan, *Traité de Chim. Minérale.*
Iron	7·2	7·8	Roberts and Wrightson, Landolt and B. P. ch. Tab.
Cobalt	6·7	8·8	Mean, Rammelsberg, *Pogg. Ann.*, 1849.
Nickel	6·6	8·9	Schroeder, 1859.
Copper	7·1	8·9	Kahlbaum and Sturm, *Zeit. f. anorg. Chem.*, 1905.
Zinc	9·2	7·1	Rammelsberg, *Monatshefte, preus. Akad.*, 1880.
Gallium	11·7	5·95	Lecoq. de Boisbaudran, 1876.
Germanium ...	13·3	5·46	Winkler, *Journ. prak. Chem.*, 1886.
Arsenic	13·1	5·7	Bettendorff, 1867.
Selenium ...	17·6	4·5	Mean. dif. vars., *Journ. f. phys. Chem.*, 1900.
Bromine... ...	27·1	2·949 (L at BP)	Ramsay, Ramsay and Masson, Thorpe. (mean)
Krypton ...	37·8	2·155 (L)	Ramsay and Travers, *Trans. Roy. Soc.*, 1900.
Rubidium ...	58·2	1·52	Bunsen, 1863.
Strontium ...	34·5	2·54	Matthiesen, 1855.
Yttrium ...	?	?	
Zirconium ...	21·8	4·15	Troost, *Compt. rend.* 61, 1865.
Niobium ...	13·2	7·06	Roscoe, *Chem. News*, 1878.
Molybdenum ...	10·6	9·1	Fused, Moissan, *Traité de Chim. Minérale.*
Ruthenium ...	8·8	11·4	Fused, Deville and Debray, *Ann. Chim. Phys.*, 1859.
Rhodium ...	8·5	12·1	Fused, Deville and Debray, *Ann. Chim. Phys.*, 1859.
Palladium ...	9·4	11·4	Fused, Deville and Debray, *Ann. Chim. Phys.*, 1859.
Silver	10·2	10·5	Various.
Cadmium ...	13·1	8·60	Kämmerer, *Berichte*, 1874.
Indium	15·1	7·421	Winkler, *Journ. prak. Chem.*, 1867.
Tin	16·3	7·29	Matthiesen, 1860.
Antimony ...	18·0	6·71	Mean of various, Moissan, *Traité de Chim. Minérale.*
Tellurium ...	20·5	6·21	Mean of various, Moissan, *Traité de Chim. Minérale.*

Element.	Atomic Vol.	Density. L = Liquid. In other cases Solid.	Authority for Density.
Iodine	25·7	4·933	Ladenburg, *Berichte*, 1902.
Xenon	37·0	3·52 (L)	Ramsay and Travers, *Trans. Roy. Soc.*, 1900.
Caesium	70·4	1·886	Graefe and Eckart, *Zeit. anorg. Chem.*, 1899.
Barium	36·6	3·75	Kern, *Chem. N.*, 1875.
Lanthanum ...	22·8	6·1	Hillebrandt and Norton, *Pogg. Ann.*, 1876.
Cerium	21·0	6·68	Mean, Hillebrandt and Norton, *Pogg. Ann.*, 1876.
Ytterbium ...	?	?	
Tantalum ...	14·1	12·79	Moissan, *Compt. rend.* 134, 1902.
Tungsten ...	9·8	18·7	„ *Ann. d. Chim. Phys* (7), 8, 1896.
Osmium	8·5	22·48	Fused. Joly and Vèzers, *Compt. rend.* 116, 1893.
Iridium	8·6	22·421	Fused, Deville and Debray, *Compt. rend.* 146, 1868.
Platinum ...	9·1	21·50	Fused, Mean, Deville and Debray, *Compt. rend.* 146, 1868.
Gold	10·2	19·32	Fused, G. Rose, 1848.
Mercury	15·7	12·764 (L at BP)	Bock, "*Trav et men d. B. Internationale des Pois-e-Mes*," 1883.
Thallium ...	17·2	11·853	De la Rive, *Compt. rend.*, 56, 1863.
Lead	18·2	11·37	Mean of various.
Bismuth	21·2	9·80	„ „ „
Radium	33·8 ?	6·7 ?	From graphic extrapolation of densities of Ca, Sr, Ba plotted against atomic weights of same elements *plus* that of Ra.
Niton	38·7 ?	5·8 ? (L)	From Ramsay and Gray's results.[1]
Thorium ...	21·1	11·0	Nilson, *Berichte*, 15, 1882.
Uranium ...	12·8	18·7	Zimmermann, *Annalen*, 232, 1886.

[1] These authors give (*Trans. Chem. Soc.* 95 (1909), p. 1,083) as the density for liquid niton near its boiling point 4·6, if the atomic weight is 176, and 5·7 for an atomic weight of 219. The figure 5·8 corresponds with the atomic weight found later by the same investigators, namely 222·4.

CHAPTER IV

THE OLDER CHEMISTRY

THE PERIODIC LAW—PART II. AND THE INERT ELEMENTS

The Periodic Law and New Elements.—Perhaps the greatest fascination which exists in science is for one of its followers to be in such a position as to make a true prophecy—to predict the unknown from the known. Think of the delight of the astronomer, when from certain erratic movements of the heavenly bodies he comes to the conclusion that a new or hitherto unknown world exists, calculates its position, and on turning his telescope to the spot finds it to be actually there.

This is very much what occurred in 1846, when Adams and Leverrier simultaneously, or almost simultaneously, predicted the existence of the planet Neptune from the perturbations of Uranus.[1]

Imagine Pasteur's triumph, who, when scarcely more than a boy, predicted that a new isomer of ordinary tartaric acid should exist, which ought to rotate a ray of polarised light to the left instead of to the right hand: thought out a method for obtaining it, and after performing the necessary operations on glancing through the polariscope at the preparation thus obtained, found that his anticipations were realised.

His charming biographer and son-in-law, M. Radot,[2] tells

[1] In 1845, Adams, who for two previous years had investigated the perturbations of Uranus, sent his completed elements to Professor Challis and to Airy, together with the statement that according to his calculations the irregularities in the motion of Uranus could be accounted for by the action of an exterior planet, of which he had calculated the motions and orbital elements.

Leverrier, in the same year, made a more extensive mathematical investigation of the subject. The planet was actually discovered in 1846 from these investigations.

[2] English translation by Lady Claud Hamilton, "Louis Pasteur. His Life and Labours." In French, "*M. Pasteur. Histoire d'un Savant par un Ignorant.*"

us "that he quitted the laboratory abruptly. Hardly had he gone out when he met the assistant of the physical professor. He embraced him, exclaiming 'My dear Monsieur Bertrand, I have made a great discovery . . . I am so happy that a nervous tremulousness has taken possession of me, which prevents me from again looking through the polariscope. Let us go to the Luxembourg and I will explain it all to you.'"

Mendeléef was among these fortunate Prophets of Science, and so also was Sir William Ramsay later. Mendeléef very soon realised after formulating the Periodic System or probably when formulating it, that if order was to be established in the law, vacant spaces or gaps must be left in the table, and that these must belong to elements not then discovered. His exact statement was as follows:—

> "The Periodic Law renders it possible for us to bring to light the properties of the new elements, whose atomic analogues are known. . . . We see from the table that many elements are missing and we can confidently predict their discovery."

His meaning as regards "atomic analogues" will be understood from the following diagram in which E is the element in question and A, A, A, A, the immediate atomic analogues:—

	Group X.	Group Y.	Group Z.
Series 3, etc.[1]		A	
Series 5, etc.	A	E	A
Series 7, etc.		A	

[1] That is to say, even or uneven series according to the position of E. (See Table, p. 54.)

On the whole, the properties of an element and of its compounds are the mean of those of its immediate atomic analogues.

Take for instance the case of selenium, which may be tabulated in relation to its immediate atomic analogues thus :—

	Gr. V.	Gr. VI.	Gr. VII.
Series 3.		S	
Series 5.	As	Se	Br
Series 7.		Te	

(1) *Atomic weight.*—To arrive at it from the means, we have :—

$$\frac{As + Br + S + Te}{4} = \frac{74 \cdot 96 + 79 \cdot 92 + 32 \cdot 07 + 127 \cdot 5}{4}$$

$$\frac{314 \cdot 45}{4} = 78 \cdot 6 \quad \text{(Actual At. Wt. } 79 \cdot 2\text{).}$$

(2) *General character of the element.*—The two atomic analogues of selenium S and Br. are well marked non-metals, while As and Te are of the transitional type. Selenium, while in most respects a non-metal, yet shows certain metallic properties. For instance, one of its modifications conducts electricity and has a metallic appearance ; it is indeed often spoken of as "metallic" selenium.

(3) *Compounds.* (A) *Hydrides.*—AsH_3. Non-fuming gas, having no well-marked acidic or basic properties. SH_2, SeH_2, TeH_2. Non-fuming gases of powerful and disagreeable odours, having slight acidic properties and precipitating many metals from solutions of their salts as sulphides, selenides or tellurides respectively. HBr. Fuming gas, having strong acidic properties.

(B) *Chlorides.*—$AsCl_3$. Liquid easily decomposed by water

into As_2O_3 and HCl. S_2Cl_2, SCl_2, SCl_4. Liquids. Only S_2Cl_2 stable; the others readily dissociate into it and chlorine. S_2Cl_2 decomposed by water into SO_2, S and HCl. Se_2Cl_2, $SeCl_4$. The first an oily liquid, decomposed by water in a similar manner to the corresponding sulphur compound; the second a solid, decomposed by water into H_2SeO_3 and HCl. $TeCl_2$, $TeCl_4$. Both colourless solids. The first decomposed by water into Te, H_2TeO_3 and HCl. The second decomposed by hot water into the same products, but giving with a small quantity of cold water an oxy-chloride.

(C) *Oxides* (Chief).—As_2O_3, As_2O_5. Both solids. The first possesses both acidic and basic properties; the second only acidic properties. SO_2, SO_3. The first a gas with strong reducing properties; the second a solid with a powerful attraction for water, with which it unites with much evolution of heat. SeO_2 (sole oxide). Solid, easily reduced to Se. TeO_2, TeO_3. Solids. Bromine forms no oxides.

(D) *Oxygen acids.*—(Chief) H_3AsO_3. Only derivatives known *e.g.*, Ag_3AsO_3, H_3AsO_4. (And the corresponding Pyro—and meta-acids). Strong acids. H_2SO_3, H_2SO_4. The first only known in solution or as crystalline hydrates. A reducing agent, and readily dissociates into water and the anhydride. The second a stable liquid with very strong acidic properties. H_2SeO_3, H_2SeO_4. The first a solid, easily reduced; the second a liquid. H_2TeO_3, H_2TeO_4. Both solids, the first nearly insoluble in water; the second sparingly soluble in cold water. Both yield the anhydrides on heating.

Before returning to Mendeléef's predictions regarding the elements which had not been discovered when he formulated the Periodic Law, it should be mentioned that by "remote atomic analogues" are meant the elements corresponding with the one in question in *consecutive* series instead of those in alternate series. Thus, in the case of selenium, chromium and molybdenum are the remote analogues.

Next, in finding names for the undiscovered elements Mendeléef selected the upper immediate analogue, and named the undiscovered element after it by prefixing the Sanscrit word for "one" or "first," namely, "eka;" or if the element had no immediate atomic analogue above it and it occupied the next lower position he employed the corresponding word for "two" or second, namely, "dwa," and so on.

The following are a few of his predictions:

Eka-aluminum. (Predicted Properties.)	*Gallium.* (Discovered 1875). (Actual Properties.)
Atomic weight about 68.	Atomic weight 69·3 ($H = 1$).
Readily obtained by reduction.	Readily obtained by electrolysing an alkaline solution of the hydrate.
Melting point low.	Melting point 30·15.
Sp. Gr. 5·9.	Sp. Gr. 5·93.
Not acted upon by air.	Superficially acted upon by air at a bright red heat.
Will decompose water at a red heat.	Decomposes water at high temperatures.
Slowly attacked by acids or alkalies.	Soluble in hot HCl. Scarcely attacked by cold nitric acid. Soluble in KHO.
Will form a potash alum more soluble but less easily crystallised than the aluminum compound.	Forms a well-defined alum.
Oxide Ea_2O_3.	Oxide Ga_2O_3.
Chloride Ea_2Cl_6	Chloride Ga_2Cl_6.

Ekaboron.	*Scandium.* (Discovered 1879).
At. Wt. 44.	At. Wt. 44·7 ($H = 1$).
Oxide. Eb_2O_3. Sp.Gr. about 3·5 with not very characteristic properties, as it forms the transition from $CaO - TiO_2$. It ought to be more basic than alumina, and its compounds should resemble in form and properties those of aluminum.	Oxide Sc_2O_3. Sp. Gr. 3·8. Soluble in strong acids. More basic than alumina. Insoluble in alkalies. Gelatinous hydrate, carbonate and phosphate.

Ekaboron.	*Scandium.* (Discovered 1879).
The sulphate not so easily soluble as that of aluminum ($CaSO_4$ and $MgSO_4$).	The sulphate a white powder, easily soluble in water. $Sc_2(SO_4)_3 6H_2O$ crystallises from the syrupy liquid.
The oxide will be intermediate in properties between alumina and magnesia.	

Eka-silicon.	*Germanium.* (Discovered 1886).
Lying between Si and Sn would be related to Ti as Zn to Ca.	
Atomic weight about 70.	Atomic weight 72·04. (H = 1.)
Grey, difficultly fusible metal, obtained by the reduction of the oxide with carbon or sodium.	Greyish-white lustrous crystalline metal. Melting at about 900 C. Obtained by reducing the oxide with carbon or hydrogen.
Scarcely acted upon by acids.	Not attacked by dilute HCl, oxidised by HNO_3 soluble in H_2SO_4.
Readily soluble in alkalies.	Soluble in alkalies.
EbO_2 less basic than TiO_2, but more so than SiO_2.	GeO_2 faint acid.
$EbCl_4$ a liquid boiling at about 100·C.	$GeCl_4$ a liquid boiling at 86 C.
EbF_4 not gaseous, and would give rise to double fluorides M_2EbF_6.	$GeF_4,3H_2O$ (?) a solid. Gives double fluorides M_2GeF_6 isomorphous with silico-fluorides. Also H_2GeF_6.
	(Germanium also gives a second series of compounds, *e.g.*, $GeO,GeCl_2$ GeS, etc.)

THE INERT ELEMENTS.

Up to the year 1892, what remained when the impurities such as water, carbonic anhydride, etc., were removed from air, was believed to consist of a mixture of nitrogen and oxygen only. Though it is a remarkable fact that Cavendish in 1785 not only suspected the presence of another substance, but actually isolated a small amount of it.[1]

[1] In point of fact, he found $\frac{1}{120}$ part of atmospheric nitrogen might be due to a foreign substance. Ramsay and Rayleigh found that the amount of the latter was about $\frac{1}{80}$.

Lord Rayleigh working between 1892 and 1894 found that the densities of "atmospheric" and "chemical" nitrogen varied beyond the limits of experimental errors. The weights of 1 litre he found varied thus:—

Atmospheric nitrogen.	Chemical nitrogen.
1·257 gram.	1·251 gram.

That is to say, by about 6 in 1,200, or some 0·5 per cent.,

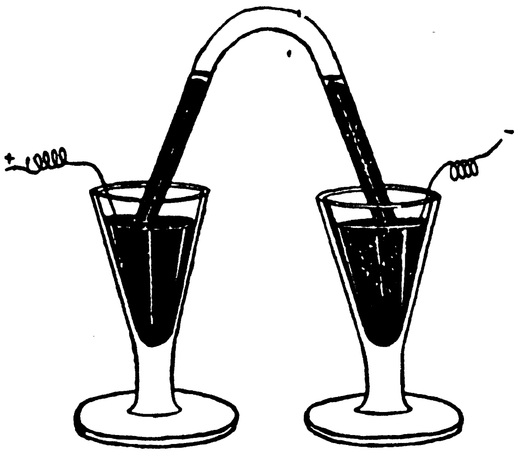


FIG. 6.—Type of apparatus used by Cavendish and Priestley.

while the accuracy of his method did not involve an error of more than 0·02 per cent.

In 1894, Rayleigh and Ramsay isolated a new element from air, which was in part the cause of the difference in the densities of nitrogen as extracted from air and from purely chemical sources respectively. Two methods were adopted for its isolation, one of which was the method employed by Cavendish in 1785. It consisted in passing electric sparks for a long time through air, confined over mercury, in presence of a solution of a caustic alkali. The diagram given above will give an idea of the apparatus he employed, and it is of interest to note that the experiment had been made ten years previously by Priestley, but not with quantitative accuracy.

A more convenient method of separating argon (as the new element was named) from air, or rather from the nitrogen obtained from air, is by causing the nitrogen to combine with a metal. Magnesium was first used, but later a mixture of magnesium and lime.

Regarding the chemical reactions in Cavendish's method, the nitrogen is fixed according to the following equations if caustic soda is used:—

$$(1)\ N_2 + 2O_2 = 2NO_2.$$
$$(2)\ 2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O$$

While in the later method, the change is:—

$$3Ca + N_2 = Ca_3N_2.$$

The isolation of argon from air presents no experimental difficulties, and can easily be shown as a lecture experiment.

The chief property of argon is its inertness. No compound of it has been obtained, and its discovery marked something like a new epoch in chemistry. Its physical properties we shall discuss later.

In 1868 Jannsen noticed in the chromosphere of the sun, during a solar eclipse, some new lines in the spectrum which had not been previously observed, and which could not be identified with those belonging to any known terrestrial element.[1]

Lockyer also studied this spectrum and attributed it to an element peculiar to the sun, and therefore named it "Helium."

Shortly after the discovery of argon, Miers, of the British Museum, drew Ramsay's attention to experiments made by Hillebrandt of the U.S. Geological Survey, on a gas, which he

[1] The so-called D_3 lines from their close neighbourhood to the D_1 and D_2 lines of sodium.

had obtained from certain minerals, and which he believed to be nitrogen.

Ramsay[1] investigated this new gas (which he obtained at first from Cleveite), and found that in addition to nitrogen, another gas was present which had an identical spectrum with Lockyer's "Helium." Ramsay and his collaborators showed that the latter was a terrestrial element, which not only occurred in certain minerals, but also in some mineral waters, *e.g.*, those of Bath, Wildbad and Cauterets, and eventually its presence was proved (by Kayser) in the atmosphere also. In its inertness it exactly resembled argon.

By methods which we shall consider presently, Ramsay showed that this new element, Helium, had an atomic weight of about 4, while that of argon he had proved to be about 40.

It could not fail to strike a man of Ramsay's mental capacity that another inert element ought to exist between helium and argon, and as President of the Chemical Section of the British Association at Toronto in 1897, he drew attention to the following relationships:—

F	O	N	C
16·5	16	17	16·3
Cl	S	P	Si
19·5	20·3	20·4	19·8
Mn	Cr	V	Ti

—the numbers referring to the differences between the atomic weights of the elements in question (vertically); and he said:—

"There should therefore be an undiscovered element between helium and argon, with an atomic weight 16 units higher than that of helium and 20 units lower than that of argon, namely 20 . . . and pushing this analogy further still, it is to be expected that this element should be as indifferent to union with other elements as the two allied elements."

[1] "Helium, a gaseous constituent of certain minerals," *Proc. Roy. Soc.* Part I., Vol. 58; Part II. Vol. 59.

He searched in every possible quarter for this undiscovered element, and to quote from another of his papers [1]:—

"Minerals from all parts of the globe; mineral waters from Britain, France and Iceland; meteorites from interstellar space; all these were investigated without result;" and he continues: "the systematic investigation of argon, however, gave a faint indication of where to search for the missing element."

For he found that argon could be separated by diffusion into a lighter and heavier portion.

The invention of an apparatus by Dr. Hampson for easily obtaining large quantities of liquid air at small expense and with little trouble, placed a new method of research in the hands of Ramsay and Travers, namely, ready access to low temperatures.

The idea occurred to them that by submitting argon to its effects, they might liquefy it and then treat it like any other volatile liquid, namely ascertain the presence or absence in it of impurities by the simple process of fractional distillation.

"Dr. Travers and I prepared fifteen litres of argon from the atmosphere with the purpose of distilling it fractionally, after liquefaction, for we knew from the researches of Prof. Olszewski of Cracow . . . that argon could be liquefied easily . . . and moreover we were in hope that by fractionating the air itself, gases of even higher atomic weight than argon might possibly be obtained. Both expectations were realized. On distilling liquid argon, the first portions of the gas to boil off were found to be lighter than argon; and on allowing the liquid air to boil off slowly, heavier gases came off at the last.

"It was easy to recognize these gases by help of the spectroscope, for the light gas, to which we gave the name *neon*, or 'the new one,' when electrically excited emits a brilliant flame-coloured light; and one of the heavy gases, which we called *krypton* or 'the hidden one,' is characterized by two brilliant lines, one in the yellow and one in

[1] "The Inert Constituents of the Atmosphere," *Popular Science Monthly*, October, 1901.

the green part of the spectrum. The third gas, named *xenon* or 'the stranger,' gives out a greenish-blue light, and is remarkable for a very complex spectrum, in which blue lines are conspicuous.

"Although neon was first obtained by the fractional distillation of argon, it was afterwards found convenient to prepare it from air. The torpedo-compressor which is used for compressing the air before it enters Dr. Hampson's liquefier, was made to take in the air which had escaped liquefaction in the liquefier; the denser portions were liquefied by compressing them into a vessel cooled by the denser fractions, boiling under reduced pressure, and consequently at a specially low temperature. This liquefied portion was again fractionated, and yielded neon: and it was not long before we discovered that helium was also present in the mixture. . . . The purification of neon and helium from argon, although a lengthy process, was not attended by any special difficulty."

But to separate helium from neon was more difficult and troublesome, and necessitated the employment of liquid hydrogen (for the production of which a special form of apparatus was devised by Travers). Under these conditions—

"There was then no difficulty in effecting the separation of neon from helium: for while neon is practically non-volatile, when cooled by liquid hydrogen . . . even that enormously low temperature is not sufficient to convert helium into a liquid. Hence the gaseous helium could be pumped away from the non-gaseous neon, and the latter was obtained in the pure state."

The Atomic Weights of the Inert Elements.—Ramsay had no chemical properties to assist him in the determination of the atomic weights of these inert elements. The determination of the equivalents of the new elements was not possible, and in atomic weight determinations the equivalent may, as we have seen, be regarded as the main girder, so to speak, in the structure.

He had to rely entirely on physical properties, and of these density of the gases was the most important.

According to Gay-Lussac's law of atomic volumes, this

density (or rather specific gravity), if referred to hydrogen as unity, is identical with atomic weight; but as we saw when discussing the subject that is only the case when the molecules of the gases consist of 2 atoms. If the molecule contains only 1 atom, like mercury, the density must be doubled to give the atomic weight; if it contains 4 atoms like phosphorus, the density must be halved, and so on.

There is, however, a physical property which enables us to determine, to a certain extent at all events, the number of atoms in a gaseous molecule.

Raising the temperature of a gas may be regarded dynamically as affecting the movements of its particles or molecules. Either there is an increase of the rate of motion of the molecule as a whole, which may be termed "translational" movement, and affects the pressure of the gas, just as a more rapidly moving projectile causes a greater pressure when it strikes a target than one which is moving less rapidly, or combined with this increase in translational movement there is an increase in the movement of the parts or atoms of the molecule, which has been called "internal" movement.

Thus two living people might have a desperate struggle at the edge of a cliff, causing them to fall over its edge, and while falling continue the struggle, thus losing energy as individuals; and yet on striking the ground they would exercise no more pressure than if the same two people before falling were dead.

It follows that the energy expended on a gas in increasing the internal movements of its molecular components does not increase its pressure, and also that less heat is required to raise the temperature of a gas having simpler constituted molecules than one whose molecules are more complex.

The heat required to increase the translational movements of gas particles is the same for the same volume of all gases under the same conditions of temperature and pressure, no

matter what the constitution of their molecules may be, and may be easily calculated, thus:—

$$1 \text{ gram molecule of a gas} = 22{\cdot}38 \text{ litres at N.T.P.}$$

$$\text{Expansion when heated } 1^\circ \text{C.} = \frac{22{\cdot}38}{273} = 81{\cdot}98 \text{ c.c.}$$

Suppose now that the gram molecule of the gas is enclosed in a cylinder provided with a (weightless) piston of 1 sq. cm. in area. When the temperature of the gas is raised from 0 to 1° C., the piston will be pushed up against the pressure of the air through a space of 81·98 cm. As the atmospheric pressure is equivalent to 1,033 grams per square centimetre, the work done by the expanding gas will amount to:—

$$1{,}033 \times 81{\cdot}98 = 84{,}685 \text{ cm. gms.,}$$

of which the heat equivalent is:—

$$\frac{84{,}685}{\text{Mechanical Eqt. of Heat}} = \frac{84{,}685}{42{,}700} = 2 \text{ cals. (nearly).}$$

If the gas is heated in a closed vessel, *i.e.* under conditions of constant volume, no external work is done, and the molecular heat is 2 cals. less than under constant pressure.

The ratio $\frac{\text{Mol. Ht. at constant P.}}{\text{Mol. Ht. at constant V.}}$ is for most diatomic gases:

$$\frac{6{\cdot}96 \text{ to } 6{\cdot}76}{4{\cdot}96 \text{ to } 4{\cdot}76} = 1{\cdot}403 \text{ to } 1{\cdot}420,$$

and for mercury (monatomic) $= \frac{5}{3} = 1{\cdot}666.$

Ramsay found this latter ratio for argon and the other inert gases, and therefore they have monatomic molecules.[1]

[1] This seems only natural, as they form no compounds, and, therefore, there is no reason why their atoms should combine together.

In the following table the more important properties of the inert elements are given :—

PROPERTIES OF THE INERT ELEMENTS.

	He.	Ne.	Ar.	Kr.	Xe.
Density of gas (H = 1)	1·98	9·96	19·96	40·78	64
Atomic weight (H = 1)	3·96	19·92	39·92	81·56	128
Density of liquid .	0·15	1·0 ?	1·212	2·155	3·52
Boiling points . .	−268·5	−239	−186·1	−151·7	−109·1
Melting ,, . .	below −270	?	−187·9	−169	−140
Critical temperatures (about)	−268	below −218	−117·4	− 62·5	+ 14·75
,, pressures (ats.)	2·75	29	52·9	54·3	57·2
Refractivity of gas .	0·124	0·235	0·968	1·450	2·368
Vol. per million of air (about)	10—20	10—20	9,370	0·05	0·006

Position of the Inert Elements in the Periodic System.—It will be seen from the preceding table that the properties of the inert elements are in agreement with the periodic law, that is to say with increasing atomic weights, the properties undergo steady change. It will be noticed that with increasing atomic weight there is an increase in the numerical values of all the figures referring to the physical properties of these elements.

Regarding their position in the periodic system, these elements are very interesting, as they form a transitional stage between the strongly electro-positive metals to the strongly electro-negative halogens. This will be seen from the following table :—

—[1]	He = 4	Li = 7
F = 19	Ne = 20	Na = 23
Cl = 35·5	Ar = 40	K = 39[2]
Br = 80	Kr = 82	Rb = 85
I = 127	Xe = 128	Cs = 133
Electrically −	Electrically neutral.	Electrically +

[1] Is it not possible that there is a fifth halogen with an atomic weight of about 3? Recently J. J. Thomson has stated that he has obtained evidence of the existence of an element of about this atomic weight.

[2] It will be noticed that the atomic weight of potassium is lower than that of argon.

It may here be mentioned that certainly one other member of the family of inert elements is known, and possibly more. These will be discussed under the subject of "Radio-activity" (Chaps. VII. and VIII.).

In conclusion, it seems but due to Ramsay to say that his researches on the inert elements rank among the classic achievements of science.

The experimental difficulties were often profound, and they were overcome by magnificent technique. The acumen he displayed in recognising a totally new type of chemical elements was a proof of the originality of his mind, and his search for the one which on theoretical grounds he anticipated must exist, with its triumphant ending, show that his experimental skill and scientific acumen were, if possible, surpassed by his energy and perseverance. Can any praise be adequate in describing the work of the discoverer who detects and isolates 1 part of a substance in about 170 million parts of the medium in which it occurs? Yet that was exactly what Ramsay did in his discovery of xenon in air.

CHAPTER V

THE NEWER CHEMISTRY

THE EFFECTS OF ELECTRICAL DISCHARGES ON GASES IN HIGH VACUA —AND AN INTRODUCTION TO THE SUBJECT OF RADIO-ACTIVITY.

THE statement that the discovery of radio-activity has effected a revolution in our fundamental ideas concerning the nature and properties of matter seems well justified.

The former view that the chemical elements are separate creations, independent of each other, is no longer tenable, nor is the belief that the "atoms" of these are indivisible particles.

On the contrary, the ancient theory of a primordial element out of which all substances have originated has been revived, and there is some reason for believing that Prout's hypothesis is to a certain extent justified, namely, that the so-called atoms are assemblages of smaller particles; only whereas Prout thought that these latter were assemblages of hydrogen particles, the present view is that the true atom or "electron" has a mass of about $\frac{1}{1700}$ that of the hydrogen atom.[1]

But still more remarkable than these radical changes in some of our fundamental ideas is the revival of the alchemical doctrine, namely that it is possible to transmute one element into another, and we shall see that this has actually been accomplished.

And lastly, a study of radio-activity has thrown light upon such matters as the real causes of chemical combination,

[1] There are, however, reasons for doubting this simple view of the nature of so-called "atoms" (see chapter IX.)

valency, and the inter-relationships of the elements which are embodied in the periodic system.

"The clue which led to the discovery of radio-activity was obtained from the study of electric discharges in high vacua: and the knowledge gained in this way has been indispensable in interpreting its phenomena."[1]

When an electric discharge of high potential takes place in air at ordinary pressures, its course is marked by a line of light in a zigzag direction, the so-called "spark" which is seen on a large scale in a flash of lightning.

On diminishing the pressure the spark first becomes longer, and if the pressure is still further diminished, it ceases altogether, and the discharge becomes continuous, a coloured

FIG. 7.—Plücker's tube.

glow filling the tube. The colour of this glow varies with the nature of the particular gas through which the discharge passes, and when examined with the spectroscope shows characteristic lines which afford a ready means for identifying different gases. By making the tube with a constricted part in the middle, the glow becomes concentrated in the narrow part and its brightness greatly increased; tubes thus constructed are called after their inventor "Plücker's" tubes.

In the majority of gases the glow is most conspicuous at a pressure of about $\frac{1}{200}$ of an atmosphere. It should also be mentioned that no matter what gas is used, there is a *blue* glow from the negative or "cathode" terminal, separated from the latter by a dark space, the blue glow being quite distinct from the characteristic glow of the gas and the two being separated by another dark space.

[1] "The Becquerel Rays and the Properties of Radium," the Hon. R. J. Strutt.

If the exhaustion is carried further, the blue glow retreats towards the anode and the dark spaces become broader; the characteristic glow of the gas grows fainter and eventually disappears altogether. Finally, at extremely low pressures the dark space extends throughout the tube and a fluorescent patch of light appears on the glass opposite the cathode terminal (which with ordinary soda glass is green) no matter where the anode may be situated.

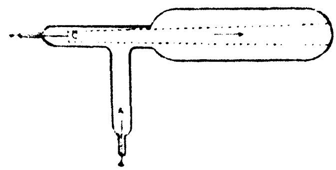


FIG. 8.—A is the anode and C the cathode. The rays from the latter travel in straight lines as shown in the figure.

The actual discoverer of these negative or cathode rays is somewhat doubtful, though the credit is usually given to Crookes who investigated them in the seventies. According to J. J. Thomson their discoverer was Plücker at a much earlier date.[1] It may be also mentioned that an explanation of their nature on a corpuscular hypothesis appears to have been first made by Varley [2] and independently by Crookes.

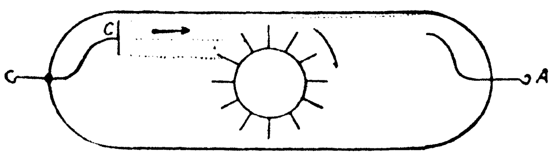


FIG. 9.—Wheel turned by cathode rays.
A the anode terminal. C the cathode terminal.

The latter showed them to have very remarkable properties and to resemble in many ways a stream of projectiles, which, as we shall see, they really are.

Thus if a small wheel with mica vanes is placed in the tube in such a way that the cathode rays strike the upper

[1] Plücker, *Pogg. Ann.*, 107, p. 77, 1859; also 116, p. 45, 1862.
[2] Varley, *Proc. Roy. Soc.*, XIV., p. 236, 1871.

or the lower vanes only, the rays behave like a stream of water in causing the movement of an ordinary water wheel.

Among other of the properties of the cathode rays the following may be mentioned.

(1) *Fluorescence.*—We have seen that the rays cause the glass on which they impinge to fluoresce with a greenish glow, in the case of the soda glass of which such tubes are generally made. The spot thus affected has the shape of the terminal from which the rays proceed. If a mica screen in the form of a cross be placed in the path of the rays, a shadow corresponding with the shape of the screen appears on the glass. If the screen is movable, then on withdrawing it the glass formerly protected is exposed to the action of the rays and fluoresces more strongly than the surrounding parts, which now show a sort of "fatigue" and do not fluoresce so strongly as at first, so that a bright green cross is seen on a duller green ground.

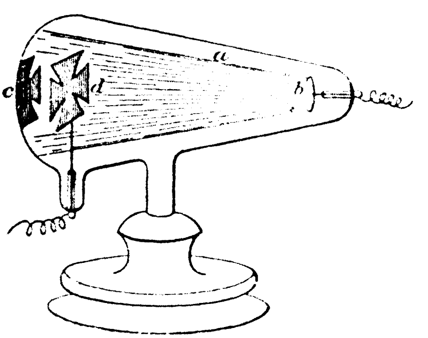


FIG. 10.—Shadow cast by mica cross in track of cathode rays.
a Highly evacuated vessel.
b Cathode terminal.
c Shadow on fluorescent glass.
d Mica cross above anode terminal.

Many other substances fluoresce with characteristically coloured light when placed in the track of the cathode rays. Thus calc spar glows with a beautiful orange red colour, rubies with a deep red, while the glow of diamonds affords a ready means of distinguishing the real from the spurious gem.

(2) *Heating effects.*—If the cathode terminal has a concave form, and a piece of thin platinum wire or sheet is placed in its

focus, on passing the current the rays are focussed on the platinum, which becomes red hot.

(3) *Chemical effects.*—These deserve a closer study[1] than apparently they have as yet received. With exceptions which will be referred to later, the observed changes have been chiefly the colouring of certain solid substances. Thus rock salt and ordinary soda glass become violet, it is said, by the liberation of sodium ions; lithium salts are also rapidly and strongly coloured. Colourless corundum crystals (alumina), it is stated, become blue, and in that way sapphires have been produced

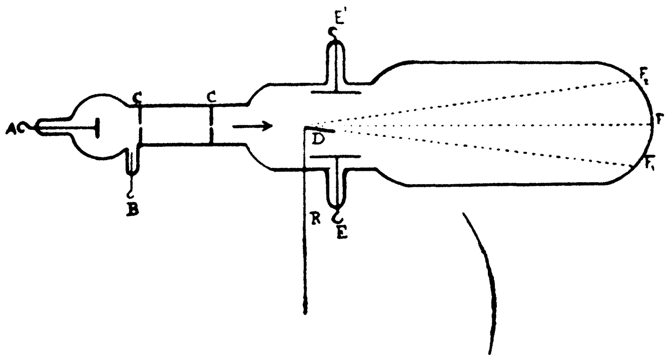


FIG. 11.—Deviation of cathode rays by a magnetic or electrostatic force.

artificially. The photographic action of the rays may also be reckoned as among the chemical changes induced by them.

The explanation formerly given regarding the phenomena observed in connection with a "Crookes' tube" was that in the latter the free paths of the gas molecules were enormously increased by the diminution in pressure, owing to the absence of collisions.

Let us consider some of the properties of the cathode rays which have led to our present ideas as to their real nature.

(1) No matter what the gas may have been in the tube

[1] See pp. 150—155; also Appendix, p. 225.

before the evacuation of the latter, we always get the same cathode rays.

(2) They are deviated or bent out of their course by either a magnetic or electric force. This is readily shown by means of the apparatus illustrated in the diagram (Fig. 11).

A is the cathode terminal and B the anode; the cathode rays (indicated by the straight dotted line) pass through the narrow slits in the metal discs C C in a straight line and impinge on the glass at F. On applying a magnet at D, the rays are deflected and impinge on the glass at F_1 or F_2, according to whether the pole of the magnet is N

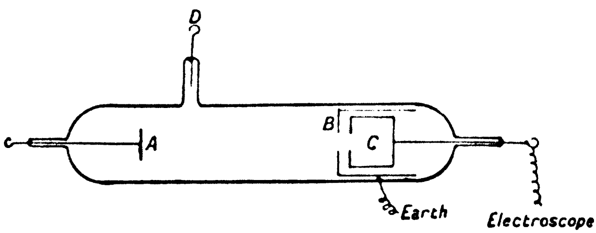


FIG. 12.—Perrin's tube.

or S. Similar effects are produced by applying an electrostatic force at E E^1.

It is thus made clear that the cathode rays consist of electrically charged particles, and from the direction of the deviation, the charge must be one of negative electricity.

This can be proved directly by an apparatus devised by Perrin[1] which is shown in the accompanying diagram (Fig. 12).

The cathode rays from A pass into the metal cylinder C after passing through a hole in the metal canister B, which latter is connected to the earth and serves to protect C from electrical disturbances. On connecting C with an electroscope and turning on the current, the electroscope is deflected in such a way as to show a negative charge.

[1] *Compt. rend.* 121, p. 1130, 1895.

The mass, velocity and electric charge of these particles, which have been termed "electrons," "corpuscles," etc., are of great importance and have been arrived at from the following considerations.

Consider a beam of cathode rays, proceeding from A (Fig. 11), as shown in the figure, and the path of which is deflected by a magnetic force applied at D at right angles to the plane of the paper. Let V be the velocity of the particles and e their electric charge. Then, since there is a deflecting force, acting always at right angles to the plane containing the path of the particles and the magnetic force, the new path of the rays will be in the direction of a circle while in the magnetic field. The radius of the circle will be the greater, the greater the mass and the higher the velocity and the smaller, the more intense the magnetic field and the greater the electric charge : or expressed mathematically :—

$$(1).\ R = \frac{M.V.}{H.e.}$$

Where

R = Radius of the circle.
M = Mass of the particle.
V = Velocity of the particle.
e = Electric charge of the particle.
H = Magnetic force.

Suppose next that an electric force X be applied between E and E^1 so as to oppose the action of the magnetic force on the cathode particle and exactly to equalise it, then the cathode beam proceeds once more in a straight line.

When the two forces are equal, we have :—

$$X.e. = H.e.V. \text{ or,}$$

$$(2).\ V = \frac{X}{H}.$$

Now all the quantities in terms of which the velocity V of

the particles is here expressed can be measured, and in this way V has been found to vary from lower to higher *vacua*, in ratios of $\frac{1}{18}$ to $\frac{1}{3}$ the speed of light, which latter is 186,000 miles per second.

Some idea of this velocity may be gathered from a comparison of the speed of a modern projectile with that of a cathode particle. While the latter would travel twenty miles, the former would only advance about one foot; and with the higher velocity the particle could travel nearly three times round the earth in one second.

Knowing the velocity of the particle, the ratio of its electric charge to its mass can be found, for by (1):—

$$\frac{e}{M} = \frac{V}{H.R.}$$

and it results from the calculation that the quotient is about seventeen millions (if electro-magnetic units be used).

Let us compare this with the same ratio for an atom, say one of hydrogen.

When water is electrolysed, a certain weight of it decomposed, is associated with a definite quantity of electricity. Each ion gives up its charge at the pole, which charge is the same for each hydrogen ion or atom, but is twice as much for each atom of oxygen, etc.

When water is electrolysed, the quantity of hydrogen evolved, no doubt contains myriads of atoms, but the ratio of electric charge to mass is the same for the multitude as for the one, and experimentally this is found to be ten thousand (if electro-magnetic units be used).

It therefore follows that the ratio $\frac{e}{M}$ for the particle or electron is 1700 times greater than that for the atom of hydrogen.

No method has been discovered for measuring the mass of

the electron, but the value of its electric charge can be determined and therefore that of its mass can be calculated.

The determination of e for the electron depends upon the fact that when a number of electrons are present in a moist gas, they serve when the latter is expanded, as nuclei for the condensation of vapour, forming raindrops, the number of which can be determined, and it is found that e has the value $1{\cdot}57 \times 10^{-20}$ electro-magnetic units (or $4{\cdot}7 \times 10^{-10}$ electrostatic units).

These figures in themselves convey no meaning, at least to the ordinary reader. What is required is the ratio of the mass of the electron to that of a hydrogen atom, and it is not difficult to arrive at this, as it has been proved experimentally that the charge on the electron is the same as the charge on the hydrogen atom. But as $\frac{e}{M}$ for an electron is equal to 1,700 $\frac{e}{M}$ for the hydrogen atom, it follows that M of the electron is equal to $\frac{1}{1700}$ M of the hydrogen atom.[1]

This opportunity may be taken for saying that electrons are formed in other ways than by electric discharges in high vacua. They are also produced :—

(1) By incandescent gases (*e.g.*, a candle flame).

(2) From heated metals and from heated carbon.

(3) From salts put into flames and in the electric spark.

(4) By the impact of ultra-violet light on metals.

(5) Emitted from radio-active substances, as we shall see later.

[1] See pp. 124—125, for the influence of speed on mass. $\frac{1}{1700}$ of the hydrogen atom is the value of the mass of slow speed electrons. Greater values of the mass were originally given, *e.g.* $\frac{1}{1000}$, but the influence of the speed was not then fully recognised. It may also be mentioned that the actual value of the mass of the electron can be found by dividing e by $\frac{e}{M}$ and is thus shown to be about 9×10^{-28} gram.

There are some other properties of the cathode rays to which attention may be directed, namely:—

(a) *Their powers of penetrating solids.* Hertz was the first to show that they can penetrate gold leaf, and Lenard went further and showed that if a thin sheet of aluminum is cemented over an opening at one end of the vacuum tube, certain of the rays pass through this aluminum "window." A better way of demonstrating the Lenard rays is to have the window within the vacuum tube, as shown in Fig. 13.

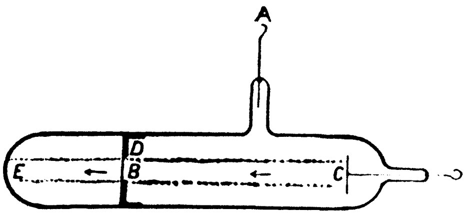


FIG. 13.—Lenard ray tube. A is the anode and C the cathode. The rays from the latter impinge on the aluminum window B cemented to the metal collar D when those having high velocities (Lenard rays) pass through the window and cause fluorescence at E.

These rays, which consist of a stream of electrons of high velocity, cannot penetrate far into air, and their penetrating powers into a medium are approximately inversely as the latter's density. Thus, gold is 15,000 times as dense as air, and therefore the same absorption is produced by a layer of gold one unit thick as by a layer of air 15,000 times thicker.

(b) *Cathode rays "ionise" gases*, that is to say, change some of the molecules into ions which enable the gases to conduct electricity.

(c) They also affect a *photographic* plate.

A second type of rays proceeds from the anode in a high vacuum. They were discovered by Goldstein and were called by him "Canal" rays.[1] They can be obtained by means of a vacuum tube constructed as shown in the subjoined diagram (Fig. 14).

[1] Goldstein, Berliner Sitz, 39, p. 691, 1886, *Ann. d. Phys.* 64, p. 45, 1898. The name (canal rays) was first given to them in 1898, and their properties described then, but their occurrence was mentioned in 1886.

C, the cathode is a perforated plate. The momentum of the canal rays is sufficient to carry them through the perforation, and like the cathode rays they produce fluorescence when they strike the glass.

By methods similar to those employed in the investigation of the cathode rays, they have been shown to consist of positively charged particles. Consequently, they are deviable by a magnetic or electrostatic force, but of course, in the opposite direction to that of the cathode rays, and the extent

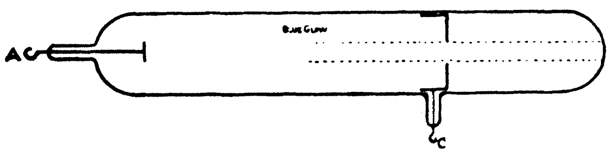


FIG. 14.—Canal ray tube. A is the anode and C is the cathode. (The canal rays do not, like the cathode rays, proceed from the electric terminal in the tube, but originate near the blue glow or even still nearer to the cathode terminal.)

of the deviation is very small in comparison with that produced on the latter.

Wien[1] showed that their mass was never less than that of a hydrogen atom and their velocities are much less than that of electrons or cathode rays. Recently Sir J. J. Thomson[2] has considerably extended our knowledge with regard to these rays. He has shown that they consist of atoms or molecules of the gases or vapours in the tube. The charges carried by these are an exact number of times (1, 2, etc.) that carried by the electron. In a few cases the charge is negative. In fact a new method of gaseous analysis has been found and some interesting facts regarding known and new groupings of the atoms have been discovered.

Yet a third class of rays is produced by electrical discharges

[1] *Ann. d. Phys.* 65, p. 440, 1898.
[2] *Phil. Mag.*, August and October, 1912. *Proc. Roy. Inst.*, 1913.

in high vacua. These were discovered by Röntgen in 1896, and are formed by the sudden stoppage of the cathode rays, the glass (as already stated) fluorescing at the bombarded spot.

In modern X ray tubes, the cathode rays are focussed on a slanting platinum target, the tubes or bulbs being provided with other arrangements as to spark gap to control the "hardness" of the rays, etc., which need not be described. Such a tube or bulb is figured in the diagram given below.

When a screen of fluorescent material, for example one coated with barium platino-cyanide (which is the material generally used) is brought near an X ray tube it lights up.

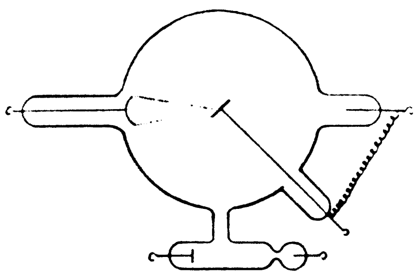


FIG. 15.—Modern "X" ray tube.

Röntgen (X) rays pass through solid materials, but their absorption is not proportional to the densities of these latter. The so-called "Radiographs" are based on this property, flesh being relatively non-absorbent, while bone is markedly absorbent. It is unnecessary to add that Röntgen rays have a powerful photographic action. They are not deflected by a magnet.

The nature of these somewhat mysterious rays is not known with certainty.

The original view was that the sudden stoppage of the charged cathode ray would give rise to vibrations akin to those of light, which are electro-magnetic in nature, and that a series of electro-magnetic pulses due to the stoppages would spread out from the anode as waves do from a centre of disturbance.

A later view is that the disturbance does not spread with a

CHAPTER VI

THE NEWER CHEMISTRY

RADIO-ACTIVITY—THE ACTIVE ELEMENTS AND THE NATURE OF THE RAYS EMITTED FROM THEM.

The Becquerel rays.—Röntgen in 1896, as already mentioned, discovered that the rays issuing from the fluorescent spot in a Crookes' tube where the cathode rays impinged on the glass, possessed remarkable properties, and these rays received the name of their discoverer.

Becquerel asked himself the question: Would fluorescence produced in other ways give origin to Röntgen rays? Now, salts of uranium fluoresce, so Becquerel[1] took a photographic plate, wrapped it in a light-tight sheath, placed some particles of a uranium salt on the sheath, and after some time found that on developing the plate he had a photograph of the salt.

"It was natural to conclude that Röntgen rays had been given off as had been thought likely.

"Extraordinary as it may seem in the face of the result this conclusion, as well as the reasoning which led to it, was quite mistaken. We now know that the fluorescence of the glass has nothing to do with the production of the Röntgen rays. We know further that the fluorescence of uranium salts is quite unconnected with the invisible rays which they emit. And lastly we know that these latter are of quite a different nature from the Röntgen rays. It seems a truly extraordinary coincidence that so wonderful a discovery should result from the following up of a series of false clues. And it may well be doubted whether the history of science affords any parallel to it."[2]

[1] *Compt. rend.* 122, pp. 420, 501, 559, 689, 762, 1086 (1896).
[2] "The Becquerel Rays and the Properties of Radium," 1904, the Hon. R. J. Strutt, p. 26.

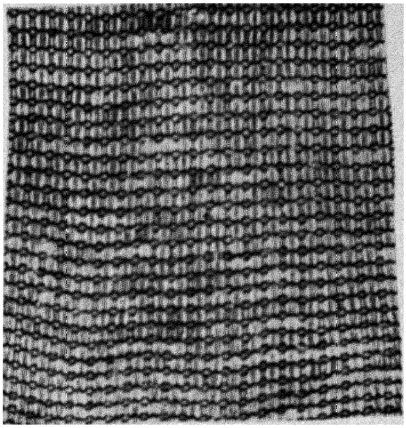


FIG. 16.—"Self" photograph of incandescent mantle.

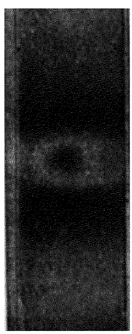


FIG. 17.—One of Becquerel's photographs of the radium rays.

Do other elements emit Becquerel rays?

Schmidt showed that compounds of one, and only one then known element did so, namely those of thorium, an element having the highest atomic weight after uranium (Th = 232. U = 238.)

It is easy to show this by means of an ordinary incandescent gas mantle which consists mainly of thorium oxide. If such a mantle is cut down the centre and flattened out on the sensitive side of a photographic plate, the whole being kept in the dark for about a week, and the plate then developed in the usual way it will be found that an exact reproduction of the mantle has been impressed on the plate. The "photograph" shown in Fig. 16 was thus obtained.

Whence comes the energy of these Becquerel rays to induce this photographic effect?

(a) Is it stored up like light in a phosphorescent substance?

No; because uranium salts over a photograph plate wrapped in an opaque coating do not affect the plate more when exposed to sunlight than in the dark.

(b) Does it come from the energy of the gas particles of the air?

This on the face of it is extremely improbable, and is disproved by the fact that a uranium salt gives out its rays in a complete vacuum.

The only other hypothesis is that uranium is slowly undergoing change while giving up some of the internal energy of the atom. It was reserved for Madame Curie[1] and her husband to trace the source of the Becquerel rays.

An examination of different uranium salts by that lady as to their power of emitting the Becquerel rays, showed that they were identical in that respect. This she did with a special electroscope of which a sketch is given in Fig. 18.

[1] M. and Mme. Curie and G. Bémont, *Compt. rend.* 127, p. 1215 (1898).

The apparatus consists of a rectangular case of brass with a clear window in front and a sheet of ground glass at the back. A metal strip A supported by the insulating material B at the top of the case is connected with a gold leaf H, and also with the metal rod C which passes through the holes in the case D and D^1, and terminates at one end in the circular and horizontal metal plate E. A similar sheet F is attached to the box at G. The radio-active material is placed on the latter (after the instrument has been charged and the gold leaf has diverged from A). This ionises the air between E and F, causing a leakage of electricity from the former, and as a consequence the gradual collapse of the gold leaf. The time required for the latter to fall through a certain angle affords a means for quantitatively measuring the activity of the material.

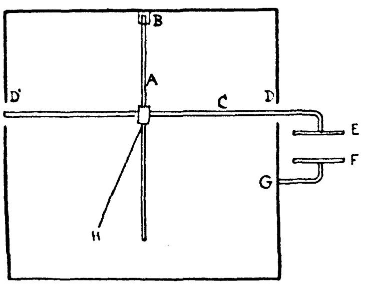


FIG. 18.—The Curie electroscope.

Mme. Curie having proved with this instrument that the same weight of uranium, no matter how combined, emitted the same amount of Becquerel rays, next tested pitchblende in the same manner, and found it to be more radiant than uranium, which is its chief constituent. How could this be explained?

Mme. Curie argued that pitchblende must contain a more active constituent than uranium, and along with her husband set herself to isolate it, using the electroscope as her guide.

Eventually in 1898 compounds of two new elements were isolated, which latter she named radium and polonium respectively,[1] and a year later Debierne isolated compounds of

[1] Polonium was the first to be discovered. Mme. Curie, *Compt. rend.* 127, p. 175 (1898).

a third from pitchblende, which he called actinium.[1] A fourth radio-active element of somewhat doubtful existence has been called "radio" lead,[2] while a fifth was discovered by Boltwood in 1907 [3] and named by him ionium.

All other commonly occurring elements have been examined, but only in the cases of potassium and rubidium has any indication been found of the emission of rays. With both of these the activity is exceedingly feeble (see footnote, p. 64).

These radio-active elements occur in excessively minute amounts, and their isolation in the form of compounds involves lengthy and tedious processes. The following scheme employed by Haitinger and Ulrich in 1908 will give an idea of one of the modern methods and the yield. It may be mentioned that they were furnished by the Austrian Government with 10,000 kgs. of residues from 30,000 kgs. of pitchblende after the bulk of the uranium had been separated from the latter. From these residues they separated nearly 3 grams of radium chloride in a state approaching purity, the work lasting two years.[4] It should be mentioned that the radium was initially present as sulphate.

Outline of Method.

The residues were washed with water to remove soluble sulphates, and then boiled with fairly strong HCl :—

Soln.	Res.
All the Po and Ac.	Heated with half its weight Na_2CO_3 (25%) solution. Mass washed to remove soluble sulphates, then HCl added. This treatment repeated three times. All the Ra now present in the acid extracts. These were precipitated with H_2SO_4; the precipitate containing the sulphates of lead, the alkaline earth,

1 *Compt. rend.* 129, p. 593 (1899); 130, p. 906 (1900).
2 *Wied. Annal.* 69, p. 83 (1899).
3 A new radio-active element. *Amer. J. of Science*, 1907, 4, 24, p. 370.
4 Monatshefte, 1908, 29, p. 485.

	Res.
	metals, radium, etc. These repeatedly heated with Na_2CO_3 sol., and the insoluble residue repeatedly warmed with HCl, and lastly with water to remove $PbCl_2$ (from which radio-lead was extracted). This process was repeated several times. Acid extracts freed from Pb by H_2S, evaporated to dryness, and the greater part of the $CaCl_2$ extracted by HCl (conc.). Crude residue weighed when moist, 20 kgs. Repeated fractional crystallisation gave two fractions, one of 2 kgs., containing most of the $RaCl_2$ (least sol.), the other of 11 kgs. containing scarcely any. By repeating the fractionation of the first fraction five portions were obtained, the least soluble of which gave an atomic weight for the metal of 225, and weighed about half a gram. Altogether, it was calculated that 3·236 grams of anhydrous $RaCl_2$ were obtained in the different fractions.

The following brief account may now be given of the new radio-active elements:—

Radium.—Owing to the small quantities of radium compounds yet isolated much remains to be learnt as regards the element.

The *metal* has been obtained by Mme. Curie,[1] and the following is copied *verbatim* from the abstracts of the *Journal of the Chemical Society*.[2]

"The amalgam was obtained by the electrolysis of a solution of 0·106 gram of perfectly pure radium chloride with cathode of mercury (10 grams) and anode of platinum-iridium. After electrolysis the solution contained 0·0085 gram of the salt. The amalgam was quite fluid, whereas with barium under similar conditions it is partly crystalline. The dried amalgam was transferred to an iron boat and heated cautiously in a quartz tube in a current of hydrogen, purified by passage through the walls of a platinum tube

[1] Mme. Curie and Andre Debierne, *Compt. rend.* 1910, 523.
[2] Abstracts II., 1910, p. 816. See also p. 119 of this book.

heated in an electric furnace. The temperature of the boat was determined by a thermo-couple. Most of the mercury was distilled at 270° C. At 400° C. the amalgam became solid, and its melting point rose progressively as the mercury was driven off to 700°, when no more mercury volatilised, but the radium itself commenced to volatilise and to attack the quartz tube energetically. The boat now contained a brilliant white metal, fusing sharply in the neighbourhood of 700°, which was considered to be pure radium. It adhered strongly to the iron and blackened immediately on exposure to the air, probably forming the nitride. A particle falling on white paper produced a blackening analogous to a burn. The metal decomposed water energetically and dissolved for the most part, showing that the oxide ('hydrate'?) is soluble. The small, black residue (nitride?) dissolved completely in a very little hydrochloric acid, showing that no mercury was present. The penetrating rays from the boat containing the metal, sealed in a glass tube, showed the normal increase following the law of the production of the emanation. Owing to the metallic radium being much more volatile than barium it is proposed to purify it by sublimation in a vacuum."

There is every reason for believing that radium is a member of the family of the alkaline earth metals. Its sulphate, chloride, bromide, and carbonate have been prepared, and resemble the corresponding barium salts. The first is even less soluble than barium sulphate: the second and third contain two molecules of water of crystallisation, as do the corresponding barium salts with which they are isomorphous, but are less soluble than the barium compounds—a property which is taken advantage of for separating radium from barium: the carbonate is sparingly soluble.

The salts of radium colour the flame of a Bunsen burner crimson, resembling in that respect compounds of strontium.

The spectrum of radium was first examined by Demarçay.[1] With a specimen that was probably nearly pure, only three strong lines of barium appeared, while the new spectrum was very bright. Further investigations of the spectrum have

[1] *Compt. rend.* 127 p. 1218; 129, p. 716; 131, p. 258.

been made by Crookes,[1] Runge and Precht,[2] Exner and Haschek,[3] and others. The following table shows the wave-lengths (W. L.) in Angström units of a few of the brightest lines of radium, together with their relative intensities, as obtained in the spark spectrum by Runge and Precht.

W. L.	Intensity.	Colour.	W. L.	Intensity.	Colour.
6200·6	10	Orange.	4533·33	10	Blue.
5958·4	10	,,	4436·49	20	,,
5813·85	15	Yellow.	4340·83	50	Indigo.
5729·2	23	,,	3814·58	100	U-Violet.
5660·81	10	,,	3649·75	50	,,
4826·12	20	Blue.	2813·84	10	,,
4682·36	50	,,			

It has already been mentioned that radium salts impart a crimson coloration to the flame of a Bunsen burner. When this flame spectrum is examined, the following additional bands and lines are easily observed:—

Bands ... 6130—6330 (Orange); 6530—6700 (Red).
Lines ... 6329, 6349 ,, 6653 ,,

The lines are all sharply defined and several of them have an intensity comparable with any known lines of other substances. Some of them can be detected in the spectrum of preparations containing even the merest trace of radium. In the final stages of the purification of radium from barium Mme. Curie used as a guide the relative intensities of two adjacent lines 4533·3 (Ra) and 4554·2 (Ba), the intensity of the latter becoming exceedingly feeble in the last stages of the purification. The bands are broad and bright but nebulous.

Finally, it may be mentioned that the general aspect of the

[1] *Proc. Roy. Soc. A.*, p. 295, 1904.
[2] *Ann. d. Phys.*, 10, p. 655, 1903.
[3] *Wien. Ber.*, 120, p. 967, 1911.

radium spectrum is similar to that of the alkaline earths, the metals of that series showing strong lines accompanied with nebulous bands.

The atomic weight of radium has given rise to controversy. Mme. Curie from analyses of the chloride, concluded that the atomic weight was 226·2 with a probable error of 0·5.[1]

Later Thorp[2] obtained the figures 226·7 (mean of three determinations).

Runge and Precht[3] from spectroscopic evidence calculated that the atomic weight should be 258, a figure differing considerably from the values previously obtained.

Marshall Watts,[4] on the other hand using another relation between the lines of the spectrum deduced much the same value as Mme. Curie. The figure now given in the International Table is 226·4.[5]

O. Hönigschmid[6] redetermined the atomic weight of radium in 1912, using as much as 1·35 grm. of the chloride. He ascertained the ratios $RaCl_2/AgCl$ and $RaCl_2/Ag$, employing the apparatus and methods of T. W. Richards. Again in 1913[7] he repeated the determination with radium bromide, using the method of Whytlaw-Gray and Ramsay of converting the chloride into the bromide, and *vice versâ*, with practically the same result. The radium salt appears to have been quite pure and free from even traces of barium. He found an atomic weight of 225·95 which is materially different from the International Table figure.

A radium salt, when freshly prepared is white, but after a time becomes yellow, and finally brown. This change in

[1] *Le Radium*, 1907, Oct.
[2] *Proc. Roy. Soc.*, 80 (1908), p. 298.
[3] *Phil. Mag.*, April, 1903.
[4] *Phil. Mag.*, July, 1903.
[5] Recently Gray and Ramsay (*Proc. Roy. Soc. A.*, 86, p. 270, 1912) obtained the value 226·45.
[6] Monatsh. 1912, 33 pp., 253—288. *Chem. Soc. Journ.* Abs. II. 1912, p. 523. (See also Chem. Soc. Annual Rep., Art. "Radio-activity.")
[7] *Nature*, 1913, p. 228.

colour is more marked with the impure salts containing barium than with the pure compounds. Solutions of radium salts show a characteristic blue luminescence which is also enhanced by the presence of barium compounds.

All compounds of radium are luminous in the dark.

The position of radium in the Periodic System is seen from the following:

Gl	=	9	
Mg	=	24	(Difference = 15)
Ca	=	40	(,, = 16)
Sr	=	87	(,, = 47)
Ba	=	137	(,, = 50)
?	=	182	(,, = 45)
Ra	=	226	(,, = 44)
?	=	271	(,, = 45)

Actinium.—Properly speaking, this is not a radio-active element, being rayless, but it gives rise to radio-active products.

It is precipitated with the group of rare earths and appears to be closely allied to lanthanum. Its oxalate is precipitated in an acid solution and is insoluble in hydrofluoric acid.

Polonium.—This is found in the bismuth separated from pitchblende residues (as already mentioned) and it so closely resembles bismuth that it is impossible, or has been found so as yet, to separate the two. Marckwald[1] obtained it by dipping a rod of bismuth into the active solution of the chloride, when the activity of the latter gradually disappeared and was transferred to the rod as a black deposit, and he called it "Radio-tellurium." When dissolved in hydrochloric acid and the solution treated with hydrazine hydrochloride, he found that all the tellurium was precipitated, while the active material remained in the solution. From 850 grams

[1] *Ber. Deutsch. Chem. Ges.* (1902), p. 2,285; also *Phys. Zeitschr*, No. 76 (1902), p. 51.

of the bismuth solution he eventually separated 0·6 gram of active material.

Rutherford has shown that this substance is identical with the polonium of Mme. Curie and also with the so-called radium F.[1]

Ionium.—This was at first mistaken for actinium. It is contained in carnotite, a uranium ore, and is so closely related to thorium that hitherto it has been found impossible to separate them. Its presence was first discovered by Boltwood in 1907.[2] It has a special interest, as we shall see later (see pp. 173—174).

Radio-Lead.—Elster and Geitel[3] found that the lead obtained from pitchblende was very active, but considered that the activity was due to admixed radium.

Hofmann and Strauss[4] also found that lead sulphate obtained from the same source was active, but that the activity was not due to foreign substances. They proposed the name radio-lead for it. It resembled ordinary lead in most of its reactions, but showed certain differences. Thus its sulphate was very strongly phosphorescent.

Giesel[5] was also able to obtain radio-lead, but found that the activity diminished with time, contrary to what Hofmann had found.

In 1904, Hofmann and his colleagues[6] showed that the lead is not itself active, but gives rise to active products.

Rutherford first,[6] and St. Meyer and v. Schweidler later,[7] appear to have proved conclusively the identity of radio-lead

[1] Paneth has recently found that polonium resembles a colloid, in that it does not pass appreciably through animal membranes or parchment paper. Radio-lead may readily be separated from it by dialysis. (*Nature*, 1913, p. 228.)

[2] *Amer. Journ. Sci.*, 24, p. 370, 1907; 25, pp. 365, 493, 1908.

[3] *Wied. Ann.*, 69, 1899, p. 83.

[4] *Ber. Deutsch. Chem. Ges.*, 1901, p. 3035.

[5] *Ibid.*, p. 3775.

[6] *Phil. Trans. A.*, 204, p. 169; *Phil. Mag.*, 8, p. 636, 1904; 10, p. 290, 1906.

[7] *Wien. Ber.* 114, p. 1195; 115, pp. 63, 697, 1906.

with radium D, which we shall consider presently, while the active products are radium E and radium F.

The rays from radium.—It will be recalled that in a high vacuum tube with an electric discharge passing through it, three different sets of rays are found, viz.:

(1) *Cathode rays.*—Consisting of "electrons," or "corpuscles." These have been proved to be minute particles whose apparent mass is about $\frac{1}{1700}$ that of hydrogen atom. These are negatively electrified,[1] and have velocities of from $\frac{1}{15}$ to $\frac{1}{3}$ that of light. They are fairly penetrating and very deviable by a magnetic or electrostatic force.

(2) *Canal rays.*—These have been shown to be particles of matter, never less than atomic in size and consisting of the gases or vapours left in the tube after its evacuation, positively electrified, velocity considerably less than that of the cathode rays,[2] only slightly deviable and with only slight powers of penetration.

(3) *Röntgen (X) rays.*—These light up screens of certain materials, *e.g.*, barium platino-cyanide; induce fluorescence in glass; non deviable; very penetrating.

How do these compare with the Becquerel rays?

It is easy to demonstrate that the latter are not all of the same kind and have unequal powers of penetration, for example:

To show this, if a little of a radium salt be placed in a metal box, on the lower plate of the Curie electroscope, the charged leaf soon collapses. If now the radium is removed, the instrument again charged, and the box containing the radium salt (but this time covered with a sheet of tin foil) be again

[1] See pp. 124, 125 for the influence of speed on the apparent mass of a moving charge.

[2] The velocity of particles of small specific gravity, such as those of hydrogen and helium, may be of the magnitude 2×10^8 cms. per second, light having a velocity of 3×10^{10}. But the velocities of heavier atoms are much less.

brought on the instrument the leaves will collapse much more slowly, say in ten times the length of time. If a second sheet of tin foil is next placed over the radium and the operations repeated, it will be found that though the additional sheet has caused some retardation, it is nothing like so great as that produced by the first.

Thus, the tin foil acts as a filter and stops the less penetrating rays, the second sheet not very materially affecting the result.

If we next place a sheet of lead, say ¼ in. thick, over the tin foil, a great reduction in the discharging effect occurs, while another sheet acts like the second tin foil layer in the first experiment. A second kind of radiation has thus been stopped out, while a third has passed through both sheets of lead. The rays from the radium compound have thus been divided into three classes, viz.:—

(1) Slightly	penetrating,	which	have	been	called	α-rays	
(2) More	,,	,,	,,	,,	,,	β-	,,
(3) Highly	,,	,,	,,	,,	,,	γ-	,,

All three types of rays (*a*) produce "ionisation" of gases, that is to say, they change some of the molecules into charged ions, and then the gases are able to conduct electricity, and (*b*) all act on a photographic plate; both of these properties being utilised for their detection and investigation. They also cause fluorescence. Thus, diamonds fluoresce with a bluish light when brought near a radium salt in a dark room, which phenomenon affords an admirable yet simple test for distinguishing the true gem from an imitation stone.

Other substances which are brilliantly fluorescent are zinc sulphide, which glows most brightly under the α-rays and barium platino-cyanide which is especially sensitive to the β and γ-rays.

The Becquerel rays also induce certain *chemical effects,*

thus, ordinary soda glass becomes violet and potash glass brown under their influence. On heating the glass, it again becomes colourless. Rock salt becomes blue. Barium salts, red. Iodine is liberated from a solution of iodoform in chloroform. We shall have occasion to consider other chemical changes induced by the rays later on.[1]

The rays from radium also produce important *physiological effects* as do the Röntgen rays, and much is hoped for in this respect, in relation to the use of radium for curative purposes, the Radium Institute having been founded with that object. It may also be mentioned that the curative properties of many mineral waters have been attributed to their radium content.

From these different properties of the radium rays, it will be seen that they closely resemble those from a Crookes' tube, and we may now inquire more particularly into their individual properties.

(1) *The β-rays.*—A very important property of these rays, which at once associates them with the cathode rays, is their deviability by a magnetic or electrostatic force. This may be demonstrated and measured (a) by photographic methods, and (b) by means of the electroscope, while it may also be shown (c) with the aid of a fluorescent screen.

The general nature of the arrangement in all three methods is much the same. A box or tube containing the radium[2] is placed so that its open end faces the photographic plate, electroscope or fluorescent screen, when a certain effect is produced on whichever of the latter is employed. On applying the deviating force (say that resulting from the use of a

[1] By measuring the radii of the halos found in certain rocks, which are formed round some nucleus of foreign material, Joly was able to show that the sizes of the circles were exactly those which would be formed if the nucleus was sending out rays. By comparing the intensities of the natural halos with those produced in the laboratory, it has been possible to estimate approximately the ages of the rock minerals in which the halos are found.

[2] A wire on which there is a radio-active deposit is frequently now used as a source of rays.

magnet), the position where the effect is produced is altered. This is indicated in the following diagram.

The effect is produced at C when there is no deviating force, but at D when the latter is applied. If the poles of the magnet be reversed, the deflection will take place in the opposite direction and thus the total deflection to be measured is doubled.

It should be mentioned that the rays are affected by the deviating force in the same way as the cathode rays, but they are not all deflected to the same extent, as will be seen from Fig. 19, and also from the copy of one of Becquerel's photographs (see Fig. 17, on plate facing p. 110.)

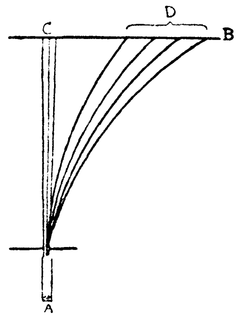


FIG. 19.—Photographic method for demonstrating the deviation of the β-rays from radium.
A. Box or tube containing the radium.
B. Photographic plate.
C. Position of rays without magnet.
D. Position of rays when magnet is applied.
(The magnetic force is applied at right angles to the plane of the paper.)

It is thus apparent that the rays consist of negatively electrified particles, which are shot out of the radium salt with varying velocities.

Their speeds and the ratio $\frac{e}{m}$ have been determined by an application of the principles already described for obtaining that ratio in the case of the cathode rays, and vary thus :—

Speed in cms. per sec.	$\frac{e}{m}$.[1]
$2{\cdot}36 \times 10^{10}$	$1{\cdot}31 \times 10^{7}$
$2{\cdot}85 \times 10^{10}$	$0{\cdot}63 \times 10^{7}$
Light $= 3{\cdot}00 \times 10^{10}$	

The particles constituting the rays are therefore moving

[1] $\frac{e}{m}$ in electro-magnetic units.

nearly as fast as light and much faster than the cathode rays.

The electron theory of matter may here be mentioned, though it is somewhat difficult to realise. Matter and electricity have the property in common of *inertia*. Both require a force to start them in motion, and both when once moving, especially at high velocities, are difficult to stop. It is this property of inertia which makes a projectile so deadly, and which causes a flash of lightning to be equally, if not more so.

The idea that matter is not material at all, but is a mere movement of the ether, was discussed a good many years ago by the late Lord Kelvin, but was revived in a different form by J. J. Thomson in 1881. Thomson showed mathematically that a moving, charged electrical sphere, must possess inertia, due to the electro-magnetic field of force it creates by its motion in the surrounding ether.

In order that this increase of inertia or apparent increase of mass should be perceptible, it is necessary that the sphere should be very small, and its speed approaching that of light. Lodge calculated that a mass = 1 when moving slowly, would become:—

Mass	Rate of motion.
1·1	50% Speed of light.
3·28	99 ,, ,, ,, ,,
5·00	99·5 ,, ,, ,, ,,
Infinite	100 ,, ,, ,, ,,

In the following table the velocities for β-rays as determined by Kaufmann are given, and the masses (M) as deduced mathematically by Thomson at these velocities are compared with those found from the ratios $\frac{e}{m}$ which were determined by Kaufmann: the masses thus calculated being

the number of times the mass of the particle with the given velocity exceeds its mass for small velocities.

V.[1]	M (Thomson).	M (Kaufmann).[2]
2·85	3·1	3·09
2·72	2·42	2·43
2·59	2·0	2·04
2·48	1·66	1·83
2·36	1·5	1·65

As a radium salt is constantly losing β-particles, and as these carry with them negative electricity, the radium salt should acquire in time a positive charge. This can be shown in a very striking way by means of an apparatus devised by R. J. Strutt and called by him "The Radium Clock" (Fig. 20, p. 126).

The tube *d* containing radium is suspended by the insulating glass rod *e* from the stopper *b* of the completely evacuated glass cylinder *a*. The radium tube is provided with a brass collar at *f*, from which two gold leaves are hung. The discharge of negative electricity from the radium salt in *d* causes these to slowly diverge from a positive charge until they touch the tin foil strips *h h* which are connected to earth. The leaves thus lose their positive charge and collapse, and this process repeats itself indefinitely, since the period of decay of radium is an exceedingly long one, thus realising as nearly as possible the idea of perpetual motion.

One other property of the β-rays may be mentioned. The cathode glow shows the spectrum of the gas in which it is produced.

Sir William and Lady Huggins photographed the spectrum

[1] Velocity in relative figures. Light = 3.
[2] *Phys. Zeitschr.*, 4, p. 54, 1903 ; *Ann. d. Physik.*, 19., p. 487, 1906.

of luminescent radium compounds and showed that it corresponded with that of incandescent nitrogen contained in the air surrounding it, thus establishing another point of resemblance between the cathode rays and the β-rays.

(2) *The a-rays.*—We owe the detection and investigation of these rays largely to the genius of Rutherford,[1] and as we shall see later, they are of extraordinary interest. It was easy to prove by the different methods already mentioned that the β-rays are deviable by a magnet, but it was very difficult, on the other hand, to show that the α-rays are also deviable, but in the opposite direction, because their deviability is so slight. This was, however, accomplished by Rutherford,[2] using an apparatus similar to that already described (Fig. 19). Another apparatus employed by him is shown in Fig. 21.

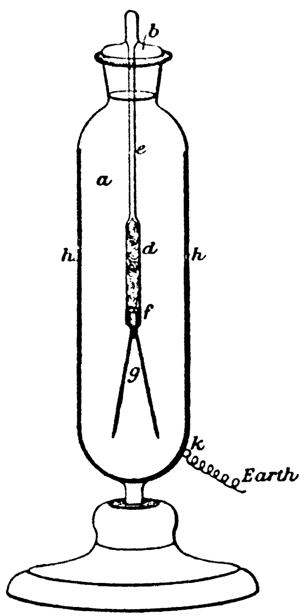


FIG. 20.—"The Radium Clock." (From Strutt's "Becquerel Rays.")

In this, the general method employed was to allow the rays to pass through narrow slits and to observe whether the rate of discharge of an electroscope, due to the issuing rays, was altered by the application of a strong magnetic field.

The rays from a thin layer of radium passed upwards through a number of narrow slits, G, in parallel, and then through a thin layer of aluminum foil, 0·00034 cm. thick,

[1] *Phil. Mag.*, Feb., 1903 ; *Phys. Zeitschr.*, p. 235, 1902, and many subsequent papers.
[2] *Phil. Mag.*, 12, p. 348, 1906.

into the testing vessel V. The ionisation produced by the rays in the testing vessel was measured by the rate of movement of the leaf of an electroscope B. The gold leaf system was insulated inside the vessel by a sulphur bead C, and could be charged by means of a movable wire D, which was afterwards earthed. The rate of movement of the gold leaf was observed through small mica windows in the testing vessel by means of a microscope provided with a micrometer eye-piece.

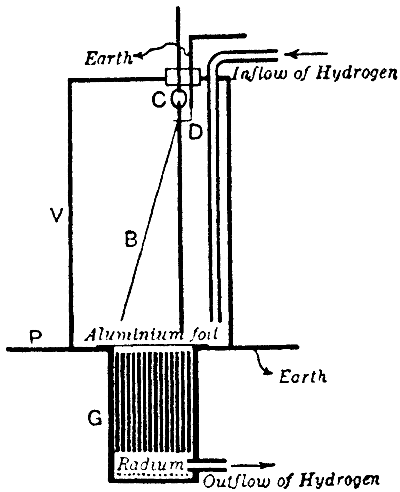


FIG. 21.—Rutherford's apparatus for investigating α-rays.

In order to increase the ionisation in the testing vessel, the rays passed through 20 to 25 slits of equal width, placed side by side.

The magnetic field was applied perpendicular to the plane of the paper, and parallel to the plane of the slits. The rays are thus deflected in a direction perpendicular to the plane of the slits, and a very small amount of deviation is sufficient to cause the rays to impinge on the sides of the plate, where they are absorbed.

The testing vessel and system of plates were waxed to a lead plate P, so that the rays entered the vessel V only through the aluminum foil. It is necessary in these experiments to have a steady stream of gas passing downwards between the plates, in order to prevent the diffusion of the emanation from the radium upwards into the testing vessel. The presence in the testing vessel of a small amount of this emanation, which is always given out by radium,

would produce great ionisation and completely mask the effect to be observed. For this purpose a steady current of dry electrolytic hydrogen, of about 2 c.c. per second, was passed into the testing vessel, streamed through the porous aluminum foil, and passed between the plates carrying the emanation with it away from the apparatus. The use of a stream of hydrogen, instead of air, greatly simplifies the experiment, for it *increases* the ionisation current due to the α-rays in the testing vessel, and at the same time greatly *diminishes* that due to the β- and γ-rays. This is caused by the fact that the α-rays are much more readily absorbed in air than in hydrogen, while the rate of production of ions due to the β- and γ-rays is much less in hydrogen than in air. The intensity of the α-rays after passing between the plates is consequently greater when hydrogen is used; and since the rays pass through a sufficient distance of hydrogen in the testing vessel to be largely absorbed, the total amount of ionisation produced by them is greater with hydrogen than with air.[1]

From the magnetic and electrostatic deflection of the α-rays, Rutherford proved that:—

$V =$ about $\frac{1}{15}$ that of light; $\frac{e}{m} =$ about 5×10^3 (electro-magnetic units).

The value of $\frac{e}{m}$ for the hydrogen atom liberated in the electrolysis of water is 10^4 (in the same units). Assuming the charge carried by the α-particle to be twice that carried by the hydrogen atom, the mass of the α-particle is about four times that of the hydrogen atom. We shall see that the question of the mass of the α-particle is one of the greatest importance, and Rutherford's further investigations on the subject will be discussed in a later chapter (see pp. 155—160).

[1] Rutherford. "Radio-activity."

A very beautiful instrument for observing an effect of the α-particles was devised by Crookes, and was called by him the "Spinthariscope." A small fragment of radium or polonium compound, or even of the mineral pitchblende, is fixed several millimetres away from a small zinc sulphide screen. Above this screen is a lens. On looking through the latter in a completely dark room, bright spots of light are seen to flash out on a perfectly dark background. The effect is like the sudden appearance of stars in a starless sky, each instantaneously disappearing to be replaced by others. These scintillations are caused by the impact of the α-particles on the zinc sulphide, each being caused by a single particle. Becquerel's opinion was that the crystals of the zinc compound are actually fractured. If two pieces of loaf sugar are rubbed together in the dark, they become luminous, probably from a similar cause.[1] We shall see later on that the actual number of α-particles expelled from a given weight of a radium salt can be counted by the scintillations which they produce.

The γ-rays.—These are the most penetrating of all the rays emitted from radium, and were discovered by Villard in 1900.[2] So penetrating are they that, using 30 mgs. of radium bromide, they will pierce an iron plate 30 cms. thick.

Like the other rays, they ionise gases, act on a photographic plate, and cause certain substances to fluoresce, *e.g.*, barium platinocyanide.

They are distinguished from the α- and β-rays by not being deviable by a magnetic or electrostatic force, and apparently are neutral electrically.

γ- and β-rays appear always to go together, and are related in their proportions.

[1] Later work has led to the belief, however, that the scintillations are due to the breaking up of the molecules or aggregates of molecules, and not to the mechanical disruption of the crystals (Rutherford, *Proc. Roy. Soc. A.*, 83, p. 561, 1910).

[2] *Compt. rend.*, 130, pp. 1010, 1178.

The available evidence shows that there can be little doubt that γ-rays are of the type of very penetrating X-rays. The hypotheses as to the exact nature of these X- (or Röntgen) rays have already been discussed. It has not yet, however, been

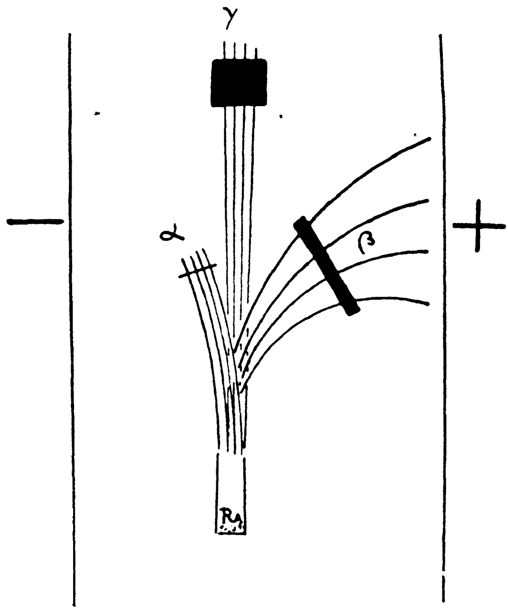


FIG. 22.—To illustrate the electric properties and penetration of the radium rays. (Somewhat modified by the author from the original Curie diagram.)

possible to obtain evidence which would enable a definite decision to be arrived at on this subject.

We may summarise the chief properties of the three types of rays emitted from radium as follows :—

(1) α-rays. Positively electrified particles whose mass is larger than that of a hydrogen atom. Slightly deviable by a magnetic or electrostatic force. Slightly penetrating. Velocity about $\frac{1}{15}$ that of light. May be compared with the canal rays of a Crookes' tube.

(2) β-rays. Negatively electrified particles of similar mass

to that of the cathode rays ($\frac{1}{1700}$ that of hydrogen atom). Strongly deviable by a magnetic or electrostatic force. Fairly penetrating. Very high velocity varying from $\frac{1}{3}$ to $\frac{9}{10}$ that of light. Resemble the Cathode rays of a Crookes' tube, but have a higher velocity.

(3) *γ-rays.* Apparently electrically neutral. Non-deviable by a magnetic or electrostatic force. Very penetrating. Velocity probably very high and approaching that of light. Exact nature unknown. Resemble Röntgen or X-rays.

Some of the above properties are illustrated by Fig. 22, part of which was suggested by Mme. Curie.

APPENDIX TO RADIO-ACTIVE ELEMENTS.

URANIUM.—Klaproth, in 1789, suspected the presence of a new metal in the mineral pitchblende (previously mistaken for an ore of zinc) to which he gave the name of uranium, from that of the planet Uranus. The metal was first isolated by Peligot in 1842.

EXTRACTION.—Pitchblende (impure U_3O_8), after being roasted to drive off sulphur, arsenic and molybdenum, is again roasted with sodium carbonate (and a little nitrate). The resulting mass (containing sodium uranate) is treated with water, and the insoluble residue with dilute sulphuric acid which dissolves the uranium. The solution is evaporated and heated to drive off the excess of acid, and the residue extracted with water which dissolves impure uranyl sulphate. To the solution of this, excess of sodium carbonate is added, and the precipitate, containing iron, aluminum, nickel and cobalt, allowed to subside; the solution is next decanted and precipitated with caustic soda, when the commercial oxide of uranium is obtained.

The *metal* varies somewhat in properties, according to the method employed for its isolation. Obtained by reducing U_3O_8 in the electric furnace, it is malleable, hard and of much the same colour as nickel and can be polished. It is permanent in the air at ordinary temperatures, but when powdered fires at about 170°. It decomposes water.

COMPOUNDS.—Uranium functions as a hexad in UO_3 and in uranyl compounds (UO_2''), also as a tetrad in UCl_4, etc., while in $U_3O_8 = 2UO_3, UO_2$ it behaves as both hexad and tetrad; its compounds are

used commercially for imparting a yellow colour and greenish fluorescence to glass. The following is a conspectus of some of its chief compounds :—

Uranic (U^{VI}).—UO_3. Action of heat on the hydrate (H_2UO_4) or on $UO_2(NO_3)_2$, yellow amorphous powder.

H_2UO_4. Heating a 2 per cent. uranium acetate solution for 100 hours in a sealed tube at 175, yellow crystals.

K_2UO_4. Yellow crystals.

$K_2U_2O_7$. Yellow precipitate.

Uranous (U^{IV}).—UCl_4. Direct synthesis or action of chlorine on a mixture of charcoal and U_3O_8. Dark green octohedra with metallic reflex : deliquescent.

UO_2 (formerly regarded as the metal and functions as the radical uranyl). Obtained by the action of potassium on uranyl chloride, as black octohedral crystals.

UO_2Cl_2. Yellow crystals.

UO_2,H_2O. Action of ammonia on UCl_4 solution.

UO_2, $(NO_3)_2$, $6H_2O$. Action of nitric acid on U_3O_8. Yellow crystals soluble in ether.

Uranoso-uranic (U^{VI} and U^{IV}).—U_3O_8 or UO_2, $2UO_3$. Green oxide. Main constituent of pitchblende.

The following are also known : UCl_5, UCl_3, UO_4.

THORIUM.—In 1818 Berzelius thought that he had obtained a new earth from a mineral obtained from Fahlun, which he called thoria, but afterwards he identified the supposed new earth as consisting chiefly of yttrium phosphate. Ten years later Esmark discovered, near Brevig, in Norway, the mineral now known as *thorite* and from the latter Berzelius obtained the true thoria.

OCCURRENCE.—The following are a few of the chief thorium minerals :—

Thorite, $ThSiO_4$, Monazite (one of the chief commercial sources). Chiefly $(CeLaDi)PO_4$, but contains from 5—7 per cent of ThO_2.

Thorianite. A newly discovered mineral, mainly ThO_2, but contains a considerable proportion of uranium oxides and smaller quantities of other oxides, *e.g.*, PbO. This mineral is remarkable for its helium content, 1 gram of it when heated yielding as much as 8·2 c.c.

EXTRACTION OF THORIUM COMPOUNDS.—(1) *From thorite.* The mineral is evaporated to dryness with strong sulphuric acid, the resulting thorium sulphate dissolved out by cold water and precipitated as a

basic salt on boiling the solution. (2) *From monazite.* The mineral is heated, as before, with strong sulphuric acid, treated with water and boiled with oxalic acid, when thorium oxalate is precipitated.

The *metal* may be obtained either by heating the double chloride of thorium and potassium with sodium, or by heating the double fluoride of thorium and potassium with potassium. It is known in two forms, viz. (a) greyish glistening powder, (b) crystalline.

It is stable in air, and does not decompose water. It unites directly with chlorine, bromine and iodine when heated in them, and in doing so glows. It is soluble in dilute hydrochloric and sulphuric acids, and in concentrated sulphuric acids, when heated, with evolution of SO_2. It is only attacked very slowly by nitric acid, and is not attacked by alkalies.

COMPOUNDS.—Thorium belongs to the same group of elements as titanium, zirconium, and cerium, but differs from them in forming an oxide, Th_2O_7. The following is a conspectus of some of its chief compounds :—

ThO_2. White powder formed on the ignition of the hydrate, $Th(OH)_4$. This oxide (thoria), with about 1 per cent of cerium oxide, constitutes the material of which incandescent mantles are made.

$ThCl_4$. Sublimes when chlorine is passed over a heated mixture of thoria and charcoal. It forms crystalline hydrates and double salts with KCl and NH_4Cl.

ThF_4, $4H_2O$. Is formed as a gelatinous white precipitate when an alkaline fluoride is added to a solution of a thorium salt.

$Th(SO_4)_2$, $9H_2O$. Colourless crystals. Forms double salts with alkaline sulphates.

$Th(NO_3)_4$, $12H_2O$. Colourless crystals.

$Th(C_2O_4)_2$, $2H_2O$. Insoluble in water.

$Th(C_5H_7O_2)_4$. Thorium acetonyl-acetone; soluble in chloroform and alcohol; can be distilled *in vacuo*; may be employed for the separation and purification of the element.

CHAPTER VII

THE NEWER CHEMISTRY.

RADIO-ACTIVITY (*continued*) — EMANATIONS, PART I. — GENERAL NATURE OF EMANATIONS — ACTIVE DEPOSITS — GRAY AND RAMSAY'S FIRST RESEARCHES ON THE EMANATION FROM RADIUM —MODERN ALCHEMY AND THE NATURE OF HELIUM.

Emanations.—As early as 1899 it was found (by Owens)[1] that currents of air disturb the radiation effects of thorium salts, as measured by electrical methods. Rutherford[2] (1900) showed that these derivatives liberate something like a gas which he termed an "Emanation." That it was of the nature of a gas, he demonstrated chiefly by the facts that it can be mingled with air, etc., blown through liquids and that its escape can be hindered by a stopper. In the same year it was discovered (by Dorn)[3] that radium evolves a similar emanation. This can be extracted from a radium salt by dissolving the latter in water, and either (a) bubbling air through the solution or (b) pumping the dissolved gases out.

The emanation thus diluted can be examined:—

(1) Electrically, when it is found to give off α-particles only.

(2) By a zinc sulphide screen which it causes to phosphoresce most brilliantly.

(3) By cooling with liquid air, when it condenses into a brilliant patch which glows in the dark.

The emanation can be collected at a given time and

[1] *Phil. Mag.*, Oct., 1899, p. 360.
[2] *Ibid.*, p. 1, Jan. 1900.
[3] Abh. d. Naturforsch Ges. f. Halle-a-S., 1900.

examined periodically with the electroscope, while its source, the solution of the radium salt, can be similarly examined.

The results are very remarkable.

The emanation when collected from the radium salt is very active, while the radium salt has lost its activity.

But while the emanation "decays" or loses its activity according to a definite law as regards time, the radium salt "recovers" or regains its activity—the curves for rate of decay and rate of recovery being complementary to each other thus:—

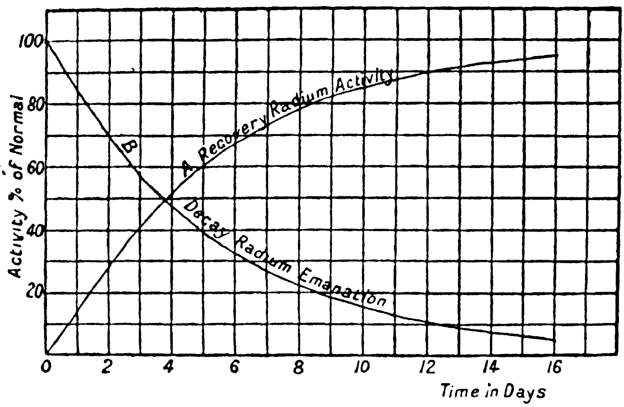


FIG. 23.—Decay and recovery curves of radium emanation (niton) and radium respectively.

Similar facts have been ascertained about other radio-active bodies.

Thus, the activity of both uranium and thorium can be precipitated by ammonia, the precipitates containing what have been called "Uranium X"[1] and "Thorium X," these

[1] Crookes was the first to show (in 1900) that when a uranium salt was precipitated by ammonium carbonate, the reagent being in excess, the small precipitate remaining was photographically active while the solution of the uranium salt separated from the precipitate was inactive. He named the active constituent "Uranium X," and showed that photographically it was weight for weight several hundred times more active than the original salt. He also showed that the active constituent differed from the inactive salt in being insoluble in ether, so that on treating an ordinary uranium salt with ether, the inactive part was dissolved while the active constituent remained.

being the active constituents, while the solutions from which they were separated are found to have lost their activity.

Both of these "X" derivatives decay, while the respective solutions recover, and according to a similar law to that governing the relations between the radium emanation and the radium salt deprived of the emanation.

Whereas, however, the "half-life" period of "Thorium X" (3·65 days) is very similar to that of the radium emanation (3·85 days), that of "Uranium X" is as much as 24·6 days.

It therefore seems impossible to resist the conclusion that thorium, radium, and other radio-active elements are spontaneously splitting up into new substances which have the characteristics of elements, or at least the chief of those characteristics from the point of view of the chemist. We shall, however, return to this matter presently.

Active Deposits.—It was discovered by the Curies[1] that the emanation (from radium) has the singular property of exciting radio-activity in any substance with which it comes in contact. This has been called "excited" or "induced" activity, and as it can be collected on any suitable surface, both its chemical and electrical properties can be investigated. This has been done, with the result that it would appear to consist of several very "transient" elements, and others of a less transient nature: these being the successive products in the transformation from the emanation to the final stage which is known at present, namely, Ra F or polonium.

The first is called "Radium A." Its "half-life" is three minutes. It emits α-rays only and chemically it behaves as a solid, is deposited on the surfaces of bodies, is concentrated on the cathode in an electric field. Volatilises at about 400—550° C., and is soluble in acids.

The second is called "Radium B." Its "half-life" is about

[1] *Compt. rend.*, 129, p. 714, 1899.

twenty-seven minutes. It emits β and γ rays and is soluble in acids. It is more volatile than A or C, and is said to precipitate along with barium sulphate.

The third is called "Radium C." Its "half-life" is about twenty minutes. It emits α, β and γ-rays, is soluble in acids, deposits on nickel and copper and volatilises at about 1000° C.[1]

"Radium C" gives rise to a branch product "Radium C_2" but in addition it passes into "Radium D" (which Ramsay and Cameron were successful in depositing from the emanation at the conical end of a very fine capillary tube, and found that "it was a grey lustrous metal, and when oxygen was admitted and the tube heated, the metallic lustre disappeared"[2]).

The "half-life" of "Radium D" is about seventeen years. It emits slow β rays, is said to be soluble in strong acids, and to be volatile below 1000° C., and is also called radio-lead. The latter in its turn becomes Ra E and this in its turn Ra F or polonium.

We shall return to the subjects of the origin and disintegration products of radium later.

Actinium X and Thorium X give rise to the other two emanations of the radio-active series, these emanations in their turn also giving active deposits, which may be collected like the corresponding deposit from the radium emanation (Niton), but best by bringing a negatively charged wire or plate into the vessel containing the emanation. On the whole the active deposits from actinium and thorium resemble those

[1] It has been shown recently that Ra C is not a simple substance, but consists of two components, C_1 and C_2—the first having a half-life period of 19·5 minutes and the second of only 1·38 minutes. So far, only very small quantities of the latter have been obtained. This is best accomplished by what is called "recoil," that is to say, by placing a negatively charged receiving plate (best in vacuo) at a short distance from the active deposit, when at the moment of its production C_2 is largely projected from the active deposit and collects on the receiving plate. This method has been used successfully in other cases, *e.g.*, in that of "Actinium D."

[2] Ramsay. Presidential address, Chem. Soc., 1909 (Trans. p. 627).

from radium, so far at least as in being soluble in acids, volatilising when heated, etc.

The following conspectus of the three active deposits may be given :—

RADIUM SERIES.

	Element.	Life period.	Rays emitted.
	Niton (Radium emanation)	5·55 Days	α
Active deposit.	Ra A	4·32 Minutes	α
	Ra B	38·7 ,,	(β),[1] γ
	Ra C	28·1 ,,	α, β, γ
	Ra C_2.	2·0 ,,	β
	Ra D (Radio-Lead) . .	23·8 Years	(β)
	Ra E	7·2 Days	β, γ
	Ra F (Polonium) . .	196·0 ,,	α

ACTINIUM SERIES.

	Element.	Life period.	Rays emitted.
	Emanation	5·6 Seconds.	α
Active deposit.	Ac A	0·0029 ,,	α
	Ac B	52 Minutes	(β)
	Ac C	3·0 ,,	α
	Ac D	6·8 ,,	β, γ
	Ac E (unknown) . .		Rayless

THORIUM SERIES.

	Element.	Life period.	Rays emitted.
	Emanation	78 Seconds	α
Active deposit.	Th A	0·20 ,,	α
	Th B	15·3 Hours	(β)
	Th C_1	84·6 Minutes	α
	Th C_2	? ,,	α
	Th D	4·47 ,,	β, γ
	Th E (unknown) . .		Rayless

[1] (β) signifies rays of very low velocity, and as a consequence easily absorbed. Such rays are spoken of as being "soft."

An account may now be given of the first investigations on the emanation from radium made by Gray and Ramsay.[1]

We have seen that it has the properties of a gas, and Rutherford and Soddy on the one hand, and Ramsay and Soddy on the other, demonstrated in 1902-1903 that in its general chemical characters it behaved like one of the inert gases, such as argon, etc. It was further shown to obey Boyle's Law and to have a definite spectrum.

Various observers sought to determine its atomic weight from its rate of diffusion, the one method then available, and results were obtained varying from 176 to 235.

In 1909 Gray and Ramsay in a remarkable research succeeded in determining many of its physical constants, and believed that they had succeeded in deducing its atomic weight from these and also its position in the periodic system.

The experimental difficulties can only be described as immense—the total volume of gas available for investigation at any time being only about $\frac{1}{10}$ cub. mm., *i.e.*, a volume considerably less than that of the head of an ordinary pin!

With this minute quantity, however, Gray and Ramsay made the following determinations :—

(1)	Melting point	$= -71°$ C. (202° abs.)
(2)	Boiling ,,	$= -62°$,, (211° ,,)
(3)	Critical temperature	$= +104{\cdot}5°$,, (377·5° ,,)
(4)	,, pressure	= 47,450 mm. (62·4 ats.)
(5)	Vapour ,, various observations	= 500 mm. at 202° (abs.) = 47,450 mm. at 377·5° (abs.)

The following are the more important details as regards the actual investigation :—

The total quantity of crystallised radium bromide available was 0·3942 grm., containing 0·2111 grm. of metallic radium.

[1] *Trans. Chem. Soc.*, 1909, p. 1073.

This was dissolved in water, the bulbs containing the solution being connected with a Töpler pump, so that the gases produced by the action of the radium salt on the water, namely hydrogen and oxygen, could be pumped off along with the emanation as often as required.

These gases, amounting on an average to 25 c.c. every seven days, were transferred to a collecting tube, coated on its interior with fused caustic potash (to absorb any carbonic anhydride), and after about an hour there, were then passed into an explosion burette (previously washed out with pure hydrogen) and there exploded. The residue consisted of the emanation and hydrogen and amounted to about 0·2 c.c. for a seven days collection. This residue was transferred to a small tube coated with fused caustic potash on the inside and the burette from which it was transferred was washed out with a little pure hydrogen (which was added to the bulk of the emanation) and the mixture transferred to the apparatus shown in Fig. 24.

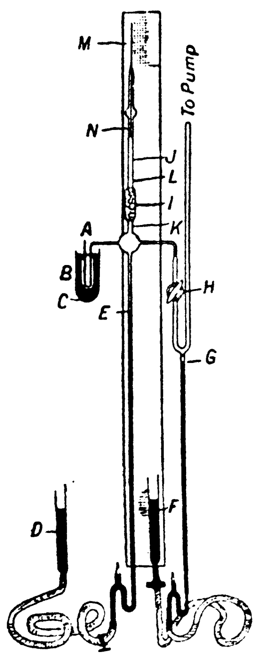


FIG. 24.—Gray and Ramsay's apparatus for investigating the radium emanation (niton).

This was done through A, with a number of precautions which need not be described. Here it was treated with pure and recently prepared quicklime to remove water and any traces of carbonic anhydride, and then cooled by surrounding the tube with liquid air in a moist paper cone at J as shown in the sketch, when the emanation solidified. The apparatus was then completely evacuated through the pump; the liquid air removed, when the emanation volatilised

and its volume read at M. Finally the tube was cut at N and mounted in a compression apparatus of the Andrews type.

Gray and Ramsay's paper may now be quoted verbatim.

RADIUM EMANATION AND THE PERIODIC LAW.

H.	He.	Li.	Gl.	N.	O.
1	4	7	9	14	16
(18)	(16)	(16)	(15)	(17)	(16)
F.	Ne.	Na.	Mg.	P.	S.
19	20	23	24	31	32
(16·5)	(20)	(16)	(16)	(44)	(47)
Cl.	Ar.	K.	Ca.	As.	Se.
35·5	40	39	40	75	79
(44·5)	(43)	(46)	(47)	(45)	(48)
Br.	Kr.	Rb.	Sr.	Sb.	Te.
80	83	85	87	120	127
(47)	(48)	(48)	(40)	(44)	(42)
I.	Xe.	Cs.	Ba.	?	?
127	131	133	137	164	169
(44)	(44)	(44)	(45)	(44)	(43)
?	?	?	?	Bi.	?
171	175	177	182	208	212
(44)	(44)	(44)	(44)	(44)	(45)
?	?	?	Ra.	?	?
215	219	221	226·4	252	257
(44)	(44)	(44)	(45)		
?	?	?	?		
259	263	265	271		

(The form of this table is different from that given in Gray and Ramsay's original paper, the vertical series here given forming the horizontal series in that paper.)

"An excerpt from the periodic table shows the probable atomic weights of the higher members of the series of which helium is the

first member . . . . . It is obviously possible to decide which of the inactive gases occupies the position of the elements with atomic weights 175, 219, and 263 by determining their vapour pressures."

This is not so obvious to the ordinary chemist until Gray and Ramsay's diagrams next given are studied.

"In Fig. 1 (Fig. 25) are shown the boiling-points and critical points

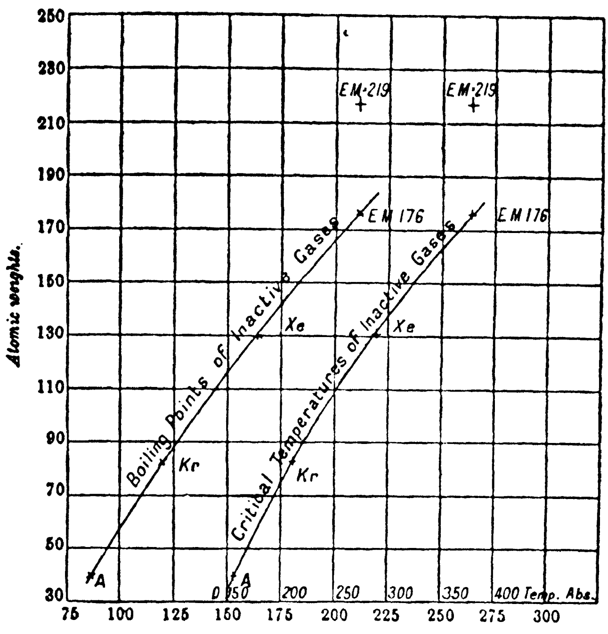


FIG. 25.

of argon, krypton and xenon plotted against molecular weights. The lines lie on the arc of a circle, and this arc, if prolonged, cuts the ordinate on which the boiling point lies at the point representing the atomic weight 176. The critical point also lies on a similar arc, and gives the same value for the atomic weight of the emanation. If, on the other hand, the atomic weight be taken as 219, that of the second element after xenon, the boiling-point would be 260 abs., 49 degrees higher, and the critical temperature, instead of 377·5, would be 430 abs.—no less than 53 degrees higher. Looking at the question

from another point of view, the boiling and critical temperatures have been mapped on the assumption that the atomic weight is 219, it is evident that in no case could curves be drawn which with any probability would pass through these points.

"Lastly, as seen in Fig. 2 (Fig. 26), the critical pressures of argon, krypton and xenon also lie on the arc of a circle having a much smaller radius than circles passing through the boiling and critical temperatures; this makes it more doubtful whether the position assigned to the emanation on the arc of this circle is justified, but if it be

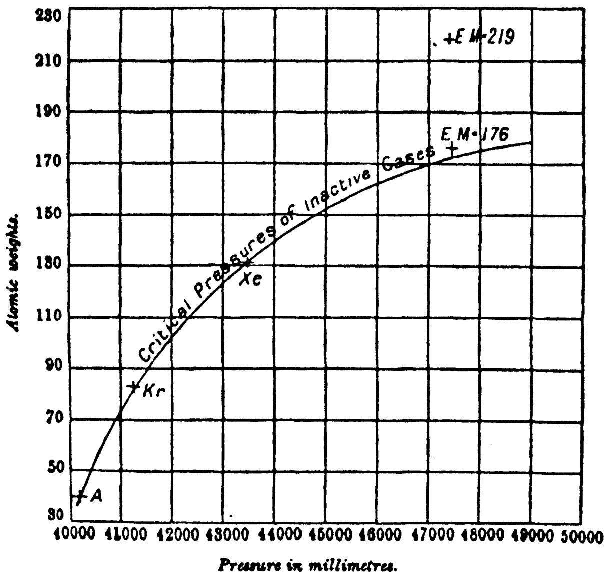


FIG. 26.

placed on the circle, the atomic weight is again indicated as approximately 176. The volume of gas obtainable from unit volume of liquid has also been measured, but it is impossible to draw any useful deduction from this ratio, for if the density of the gas be taken as $\frac{176}{2}$, the liquid has a density which places it on a point on the almost straight line joining the densities of liquid argon, krypton and xenon mapped against the atomic weights nearly on the 176 ordinate. If, however, the liquid be assumed to be derived from a gas of density $\frac{219}{2}$, its density is proportionately higher, and it fits the curve at a point where the 219 ordinate intersects it."

It may be at once stated that, for reasons to be given presently, Gray and Ramsay abandoned the atomic weight of 176 for the emanation and eventually found a much higher figure.

Properties of the liquid emanation.—"The liquid emanation is colourless, and transparent as water when seen by transmitted light; it is, however, phosphorescent and shines with a colour varying with the nature of the glass tube in which it is confined; it might be more correct to say that it causes the glass to phosphoresce. The colour varies from lilac to blue; in silica it is blue; in lead-potash glass, bluish-green, and in soda glass lilac. When compressed strongly in soda glass, the colour reminds one of the cyanogen flame, at once blue and pink. On cooling further the liquid solidifies, and ceases to transmit light; on warming it again becomes transparent. This gave a means of determining its melting point, using a pentane thermometer, which registered correctly at 78·3. The actual temperature at which the emanation melts is 71."

Properties of the solid emanation.—"On further cooling with alcohol cooled with liquid air, the colour of the phosphorescence changes. The solid glows with great brilliancy, like a small steel blue arc light. Further reduction of temperature changes the colour to yellow, and in liquid air it is brilliant orange red, the colour change takes place in inverse order on warming. The red phosphorescence disappears pretty sharply at 118 degrees. All these phenomena were observed with a microscope the objective of which was about one inch focal length."

Spectrum of the emanation.—First mapped in 1904 by Ramsay and Collie, and later in 1908 by Rutherford and Royds, also by Cameron and Ramsay and finally by Watson,[1] shows about 60 characteristic lines.

Other properties of the emanation.—(1) *Evolution of energy.*—Recent work (in Exner's laboratory at Vienna) indicates that the heat evolution per gram of radium is 118 calories per hour, and Rutherford has shown that the emanation, with its rapidly decaying products (which will be considered presently),

[1] Watson, *Proc. Roy. Soc.*, 1909, A. 83, 50—61.

evolves a quantity of heat about $\frac{3}{4}$ of that evolved by the radium from which they are derived, or nearly 90 cals. per hour.

(2) *Emission of rays.*—The emanation emits α-rays only.

(3) *Chemical actions.*—These have been investigated mainly by Ramsay alone with his collaborators. The following changes have been proved.

(a) It decomposes water into hydrogen and oxygen, but there is always an excess of hydrogen over the theoretical quantity, amounting to about $5\frac{1}{2}$ per cent. Apparently this is due to simultaneous production of hydrogen dioxide.

(b) Conversely hydrogen and oxygen combine when in contact with the emanation.

(c) Ammonia splits into nitrogen and hydrogen.

(d) Hydrochloric acid into chlorine and hydrogen.

(e) Carbonic anhydride, into carbon, carbonic oxide and oxygen.

(f) Carbonic oxide, into carbon, carbonic anhydride and oxygen.

It will be seen that many of these actions are the same as those brought about by electricity, and we know that the emanation is continuously giving off α-particles, and that these have enormous "ionising" powers.

"If we suppose that a mixture of hydrogen and oxygen is bombarded with α-particles so that charged ions of both gases are produced, partial combination of the two gases is rendered certain. The effect of liberation of particles in water might be expected to be much greater. Compare the effect of a charge of gun-cotton exploded in a confined, and in an open space. The collision disrupts innumerable molecules of water, producing charged atoms of hydrogen and oxygen. Some of these recombine. The part that escapes recombination produces the changes in volume which are actually measured" (Ramsay and Gray).

However, some of Ramsay and Gray's results do not quite fit in with this explanation (as they indeed draw attention to),

so that the exact mechanism inducing the chemical changes brought about by the emanation is not known with certainty. This much, however, seems beyond doubt from Ramsay and Cameron's quantitative results, *that whenever the emanation produces chemical action*, then, other conditions being unaltered, *each particle of emanation as it disintegrates produces the same amount of change* (Ramsay and Cameron).

Helium from Radium.—We must now retrace our steps, chronologically speaking, to the years 1903—1904, when perhaps the most startling discovery—at least from the chemist's point of view—yet made in connection with radium resulted from Ramsay and Soddy's investigation of the emanation.

In 1902 Rutherford and Soddy[1] had concluded that the emanation from thorium "is a chemically inert gas analogous to the members of the argon family," and in their paper they say "the speculation naturally arises, whether the presence of helium in minerals and its invariable association with uranium and thorium may not be connected with their radio-activity?"

A year later Ramsay and Soddy[2] published a memorable paper on "Radio-activity and the Production of Helium from Radium."

"The maximum amount of the emanation from 50 mgs. of radium bromide was conveyed by means of oxygen into a U tube cooled in liquid air, and the latter was then extracted with the pump. It was then washed out with a little fresh oxygen, which was again pumped off. The vacuum tube sealed on to the U tube after removing the liquid air showed no trace of helium. The spectrum was apparently a new one, probably that of the emanation, but this has not yet been completely examined, and we hope to publish further details shortly. After standing from the 17th to the 21st inst. the helium spectrum appeared, and the characteristic lines were observed identical in position with those of a helium

[1] *Phil. Mag.*, 1902 [VI.], 4, p. 581. *Ibid.*, 1903 [VI.], 5, p. 457.
[2] *Proc. Roy. Soc.*, 72, p. 206. *Ibid.*, 73, p. 346.

tube thrown into the field of vision at the same time. On the 22nd the yellow, the green, the two blues and the violet were seen, and in addition the three new lines also present in the helium obtained from radium. A confirmatory experiment gave identical results."

Ramsay and Soddy returned to the subject in a paper read in 1904, confirming their previous results, with an additional and important observation, viz., that the emanation suffers an enormous contraction on keeping—amounting in four weeks to about 97 per cent. As other observers have confirmed the production of helium from radium, and Debierne has also obtained it from actinium, *there can be no possible doubt that the correctness of the alchemical idea has been demonstrated, viz., the possibility of one element giving origin to another.*

It was but natural that Ramsay should follow up this matter and ask himself the question, May not other elements or their compounds be smashed up—so to speak—under the bombardment of the α-rays and give rise to different elements?

Accordingly he submitted various substances to the action of the emanation, with some very remarkable results. And in this connection the author may quote from Ramsay's Presidential Address to the Chemical Society in 1909.

"Owing to the fact that during this transformation (*i.e.*, radium into helium) the energy evolved is in the most concentrated form known, and that the emanation from radium is fairly easily soluble in water, and therefore in aqueous solutions, the action of the emanation on a solution of copper sulphate and nitrate was investigated, glass vessels being employed. Four experiments were made, each one in duplicate ; the duplicate was in each case treated like the solution containing emanation. The only difference was that the duplicate solutions contained no emanation. From the emanation solutions a larger residue was obtained in each case than from the duplicate, and while the residue from the emanation solutions showed a trace of lithium, those from the duplicates failed to give spectroscopic evidence of that metal. The fact of the experiments having been carried out in duplicate renders inapplicable

the criticisms of Prof. Hartley, that inasmuch as lithium is a widely distributed element, accidental contamination is probable. But the alleged repetition of the experiments by Madame Curie and Mlle. Gleditsch, in which, using platinum vessels, they obtained no greater residue, and no trace of lithium, cannot be explained away. There are two possible replies: either the conditions of experiment varied, so that the same result was not obtained, or it is conceivable that in presence of emanation and a copper solution, a trace of lithium was dissolved from the glass vessel (which had been tested for lithium, however, with a negative result), which escaped solution in the absence of emanation on the one hand, or in the absence of copper on the other. For emanation in presence of distilled water in a vessel of the same glass gave a minute residue in which the spectrum of lithium was not to be observed."

After discussing the effect of the emanation on a solution of silver nitrate, which gave a negative result, Ramsay continued:—

"I have, however, stumbled across a case of apparent transformation; while working in a totally different direction, the idea occurred that thorium should also yield helium. Now the radioactive constant of thorium is only the $\frac{1}{180000}$th part of that of radium; hence the necessity of working with a very much larger quantity over a very much longer time.

Miss Burke was so good as to purify for me 270 grms. of thorium nitrate. On December 20, 1905, it was dissolved in 300 c.c. of water and introduced into a round bottomed flask, provided with a capillary neck, on which was sealed an excellent stopcock. The stopcock was greased, and after the flask had been evacuated with a Töpler pump, the tap was closed."

Ramsay then describes how, after various precautions, the bulb was completely and repeatedly evacuated, the stopcock closed, and inverted in a vessel of water, where it remained altogether for three years. On examining it periodically during this time, gas could be pumped off and must have been produced. It amounted in all to more than 12 c.c. and contained small quantities of hydrogen and oxygen, large quantities of nitrogen, *and appreciable quantities of carbonic*

anhydride, which Ramsay concludes was generated from the thorium nitrate, or in other words, that one of the degradation products of thorium is carbon, which is in the same group of elements in the periodic table. The presence of helium in the evolved gases was questionable, but on the whole probable.

In another paper Ramsay, in collaboration with Usher,[1] described experiments conducted in a similar manner upon solutions of the salts of other members of the carbon group of elements. These solutions remained in contact with the emanation for four weeks, and the results were eventually calculated to represent the weight of carbon (as carbonic anhydride) produced by the action of 1 cubic mm. of the emanation. The following figures are given :—

Soln. of –	H_2SIF_6,	$Ti(SO_4)_2$,	$Zr(NO_3)_4$,	$Th(NO_3)_4$,	$Pb(ClO_3)_2$.
Yield of carbon in mgs.	0·518	0·982	1·071	2·93	0·102
			0·873	0·968	
			2·93		

Mercurous nitrate gave no trace of carbon dioxide or monoxide. The authors conclude with the remarks :—

"It is apparent from the above numbers that the elements of the carbon group, without exception,[2] yield carbon compounds under the action of the emanation ; the quantities obtained are not, however, the same. It is not improbable that those elements having a higher atomic weight are more readily decomposable (*spaltbar*) than those with lower atomic weights ; it is, however, conceivable that lead is especially stable and possesses little tendency to change itself into carbon."

Another probable instance of the production of one element from another is mentioned by Sir Wm. Ramsay.[3] It was ascertained, he tells us, that when the emanation from radium acts on water, in addition to the oxygen and hydrogen produced

[1] *Berichte d. Deutsch. Chem. Ges.*, 1909, p. 2930.
[2] Cerium compounds were not apparently included in their experiments.
[3] "Elements and Electrons," pp. 159, 160.

from that substance (p. 145), helium and neon were also found. The helium, no doubt, was produced by the disintegration of the emanation and of its active deposit, but Ramsay is convinced that the neon owed its origin to the same source, or partly so at all events.

It was, however, urged by others that the neon observed was due to a leakage of air into the apparatus, as with proper precautions neon can be detected in very small quantities of air.

Ramsay's attention, he tells us, was again directed to the subject, when he discovered in the course of the analysis of the gases escaping from the King's Well at Bath, that while the argon present in them only amounted to three quarters of the volume of that found in air, the volume of helium was 60 times and that of neon 180 times as great. In this case also the helium content could be explained by the presence of radium in the water; "unless, however, water plus niton [*i.e.*, radium emanation] gives neon, the very large quantity of neon was inexplicable."

Another experiment was therefore made on the action of niton on water, and neon was found in such an amount as would have involved the leakage of 4 c.c. of air into the apparatus, while, so far as was known, no leakage whatever occurred.

Ramsay then states, "It may therefore be taken for granted that when niton disintegrates in presence of water, neon appears; whether as a disintegration product of niton, or as the product of the action of niton on water cannot be ascertained."

In this same book[1] Ramsay mentions another experiment, in which both neon and helium were apparently produced. The glass of four X-ray tubes, stained purple by long use, was broken up, placed in a hard glass tube, which was then

[1] *Loc. cit.*, p. 162.

completely evacuated and repeatedly washed out with pure oxygen, so as to remove all traces of air adhering to the glass. The tube was then heated and the gases pumped out and examined, when both helium and neon were found, the latter, however, in very minute amount.

He also describes an experiment made by Prof. N. Collie, in which precipitated calcium fluoride was bombarded for several days with cathode rays in presence of traces of pure oxygen. The gases were then pumped out and examined, with certain precautions which need not be described, and were found to consist of carbon monoxide (which was continuously produced), silicon fluoride, oxygen and *pure neon*, but *no* helium.

A very remarkable outcome of this work has been recorded recently in a joint paper by Collie and S. H. Patterson[1] and in connection with this matter it may be mentioned that whereas Prof. Collie directed his attention to it from the chemical standpoint in relation to the origin of the neon in the experiments mentioned above, Mr. Patterson quite independently approached it from the purely physical side in relation to electronic mass, his idea being that if it were possible to increase the electric charge on the "seat" of mass of the hydrogen ion two-fold "an α-particle might be produced, in which case it would be possible to convert a hydrogen atom into one of helium."

It should also be stated that the two experimenters did not at first know that they were working on similar lines and that it was not until the later stages of their separate investigations that they became aware that they were obtaining similar results, when they then decided to co-operate.

Prof. Collie it may be mentioned, was led to investigate the

[1] "The presence of neon in hydrogen after the passage of the electric discharge through the latter at low pressures." *Chem. Soc. Journ.*, 1913 (Trans.), p. 419.

action of cathode rays on minerals such as sodalite and fluor spar from the change in colour which they then experience, and he observed that at the same time much gas was given off.

Regarding the first of these phenomena, he found that in the case of calcium fluoride (both natural and artificial) the change, which is superficial, is probably due to the liberation of metallic calcium, for if the purple mass resulting from the bombardment of the mineral by the cathode rays is placed in moistened red litmus paper, the latter burns blue.

As to the second, the evolution of gas was so considerable that a week's bombardment of the calcium salt by the rays resulted in an evolution of between 3 and 4 c.c. of gas, which consisted for the greater part of carbon monoxide though neon was also proved to be present.

An experiment was then performed in which carefully cleaned glass wool was bombarded with cathode rays, when again neon appeared among the gases pumped off.

The glass wool was then removed from the tube and pure hydrogen was admitted (3—4 c.c.) and afterwards pumped off, the tube being heated during the operation; the hydrogen was then removed by explosion with pure oxygen and the latter in its turn removed by charcoal cooled with liquid air, when again neon was found. It may now be well to quote Prof. Collie's own words:—

"It was then obvious that either the neon was being formed in the tube during the experiment, or that in some way air had leaked into the tube or the pump during the experiment. That air had leaked into the pump was rendered highly improbable, for always at the end of a day's experiments a phosphorescent vacuum was left in the tube and no change was found on examining the apparatus on the next day or the next but one. Moreover a vacuum tube was in connexion with the tube and the minutest trace of air would have meant a spectrum of nitrogen in the vacuum tube."

Collie then experimentally inquired into various possibilities, such as:—

(1) The presence of neon in the hydrogen or oxygen used in the experiments.

(2) The presence of the same gas in the glass of the tubes in which the bombardment with the rays occurred.

(3) Presence of the same gas in the (aluminum) electrodes.

All experiments on these lines gave negative results.

There still remained the possibility that although glass was found not to be porous to neon (from the air) when heated to its softening point, it might be so when subjected to a cathode discharge.

In the next experiments therefore a tube was so made that the negative electrode was jacketed with another tube, and in the first of the experiments the latter was partly filled with neon and the current passed for six hours, while in the second it was treated similarly with helium, the current being run for four days.

In neither of these experiments was there any evidence of the slightest leakage of gas from the outer to the inner tube, while neon appeared as before in the latter.

In another experiment, the inner tube was completely surrounded with another, the latter being exhausted so that no spark would pass: the inner tube as before contained hydrogen and the bombardment with cathode rays was continued for two days.

As a matter of curiosity Collie then washed out the outer tube with 1 c.c. of oxygen, which he then pumped out.

"It gave a very faint explosion (hydrogen) when a spark was passed through it in a eudiometer. The residual oxygen was then treated with cooled charcoal. The residue that remained was about fifty times as great as the residue from the inner tube and when examined *it was mostly helium with enough neon present to give the neon spectrum.*"

Collie concludes his part of the paper by stating that in all thirty-five experiments were made and that neon was found in greater or less quantity every time.

Patterson worked on very similar lines and in fifteen experiments in which hydrogen (at very low pressure) was bombarded with cathode rays, neon was found; while in four cases helium could also be detected.

In blank experiments all the operations were gone through except the bombardment with cathode rays and no neon nor helium could be detected—even when so much as 200 c.c. of hydrogen were operated upon.

Collie's experiment with a vacuous outer tube was also repeated and the production of helium in it confirmed. In a modification of this experiment, the outer tube, instead of being vacuous, contained oxygen at a pressure of 15 mm. and the inner one, hydrogen, at a pressure of 2 mm. At the end of the experiment, on removing the oxygen, the residue when examined spectroscopically was found to consist of almost pure neon with a little helium. In these last experiments, the residue in each case amounted to as much as about 1 cub. mm. of gas, which was ten times as much as Gray and Ramsay could collect at one time of niton, and with that quantity (*i.e.* $\frac{1}{10}$ cub. mm.) they made the two important inquiries on that gas already described.[1]

Collie and Patterson are not willing in the above paper, to suggest the possible sources of origin of the neon and helium obtained in their independent experiments but to those who like the author of this book are acquainted with the exceptional experimental skill of the first of these observers, the idea that either of the two gases made their way into the apparatus from extraneous sources appears to be practically impossible: and if that is the case it would seem that either (1) there has been

[1] See p. 139.

a change of one element into another or others or (2) that matter has in point of fact arisen out of energy (or ether ?).

These researches appear to open up a new and probably a fruitful field of investigation.

We must now inquire more particularly into the fate of the radium atom and the relationships of that atom to the emanation, the α-particle and helium respectively.

From the chemist's point of view, radium is an element, with a definite atomic weight, a definite spectrum, a definite position in the periodic system, etc.

And again, speaking entirely from the chemist's standpoint, it gives origin spontaneously to a gas which also has the characteristics of a chemical element, to the extent at all events of a definite atomic weight: while from this gas or "emanation" a second gaseous element, namely helium, originates, and eventually a solid metallic-looking substance in addition, which has been named "radium D," and which (as already stated) has been seen and collected by Ramsay and Gray.

Now Rutherford, in 1906,[1] carefully considered the evidence as to the connection between the α-particle and the atom of helium. All the radio-active elements eventually expel α-particles, which are identical in all respects save initial velocity, and Rutherford pointed out that whatever its nature, the α-particle must be a fundamental constituent of the atoms of all the radio-active elements.

We have seen (p. 128) that from his determinations of $\frac{e}{m}$ for the particle, Rutherford showed that if it carried twice the charge of the hydrogen atom as obtained by electrolysis, its mass would be four times as large as that atom.

[1] *Phil. Mag.*, August, 1906

Among the possibilities then discussed by Rutherford were: (1) that the α-particle is the helium atom with twice the ionic charge or (2) half the chemical atom carrying the single charge. The first of these was the one he favoured.

In 1908 Rutherford again returned to the subject in collaboration with Geiger.[1]

By measuring the charges carried by the α-particles expelled from a known quantity of radium in the form of a thin film (four times as many α-particles would have been expelled from the same weight of radium in equilibrium with its products, but the presence of β-rays would influence the result) and assuming that the α-particle carries the same charge as an ion, a value for the total number of α-particles expelled per second from 1 gram of radium had been previously calculated. If it were assumed, however, that the charge carried by an α-particle is twice as great as that carried by the ion, then the calculated number of the α-particles expelled from the 1 gram per second would have to be halved.

It follows that if the number of α-particles which are expelled in a given time from a definite weight of radium can be counted, the question of their electric charge can be decided.

Two methods of doing this suggested themselves, viz. :—

(1) An α-particle on striking a screen of zinc sulphide produces (as we have seen) a flash of light or scintillation, and with the aid of a microscope it is not very difficult to count their number per second on a screen of known area when exposed to a source of the rays. But Rutherford and Geiger point out that no confidence can be placed in this method until its results have been verified by one of an independent character and free from uncertainties, such as the

[1] *Roy. Soc. Proc. A.*, 1908, p. 141.

possibility that, owing to lack of homogeneity in the screen, only a certain number of the α-particles produce scintillations. They therefore resorted to a second method.

(2) In this recourse was had to a means of automatically magnifying the electrical effect due to a single α-particle, which had been worked out by Townsend and depended upon the effects of a strong electric field upon the gas with which the α-particles come in contact.

In Rutherford and Geiger's experiments to detect a single α-particle an arrangement was employed in which the

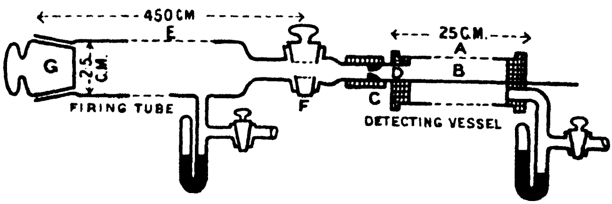


FIG. 27.—Rutherford and Geiger's apparatus for counting α-particles.

particles could be "fired" through a gas at low pressure exposed to an electric field somewhat below the sparking value.

"In this way the small ionisation produced by one particle could be magnified several thousand times. The sudden current through the gas, due to the entrance of an α-particle in the testing vessel, was thus increased sufficiently to give an easily measurable movement of the needle of an ordinary electrometer."

The apparatus they employed is shown in the above diagram.

The detecting vessel consisted of a brass cylinder A, with a central insulated wire B, passing through ebonite corks at the ends. The cylinder, with a pressure gauge attached, was exhausted to a pressure of 2—5 cms. of mercury. The central wire was connected with one pair of quadrants of a Dolezalek electrometer, and the outside tube to the negative terminal of a large battery of small accumulators, the other pole of which was earthed. In the ebonite cork C was fixed a short glass

tube D, in the end of which was a narrow circular opening. This opening, through which the particles entered the testing vessel, was covered with a thin sheet of mica, tightly waxed over the end of the tube. In most experiments the thickness of mica was equivalent, as regards stopping power (of the α-particles), to about 5 mm. of air at atmospheric pressure. Over the tube D was fixed a wide rubber tube, to the other end of which was attached a long glass tube E. A large stopcock F, with an opening 1 cm. in diameter, was attached to the end of the glass tube next to the detecting vessel. The other end of the long glass tube was closed by a ground stopper G. After making certain adjustments as to the voltage applied to the testing vessel, etc., the radio-active matter, in the form of a thin film, was introduced into the firing tube in such a way that it could be moved to any required distance from the stopcock F by means of an electro-magnet applied externally. The stopcock G was then inserted and a complete vacuum established in the firing tube.

So long as F was closed no α-particles could enter the detecting vessel, and the steadiness of the electrometer needle could be tested at intervals during the experiment. On opening the stopcock a small number of the α-particles expelled per second from the radio-active material passed through the mica plate. The distance of the active matter from the stopcock was usually arranged so that from three to five particles entered the detecting vessel per minute, each causing an average deflection of the electrometer needle of about ten scale divisions. As the needle took some time to come to rest, a larger number could not be conveniently or accurately counted.[1]

Rutherford and Geiger not only experimented with radium

[1] An improved method, making use of a string electrometer and photographic registration of the deflections (Geiger and Rutherford, *Phil. Mag.*, XXIV., 618, 1912) enables the counting of the α-particles entering the detecting vessel at the rate of 1,000 per minute.

and its products, but also with uranium, thorium, and actinium, with concordant and satisfactory results. A series of experiments was then made to determine as accurately as possible, by this electrical method, the number of α-particles expelled per second from 1 gram of radium, and the number finally arrived at was $3{\cdot}4 \times 10^{10}$. The same weight of radium in equilibrium with its products would give $13{\cdot}6 \times 10^{10}$ α-particles per second.

This result was then compared with that obtained by counting the scintillations produced by particles on a zinc sulphide screen, and good agreement was obtained between the two methods, regarding which they remark that it "brings out clearly that within the limit of experimental errors each α-particle produces a scintillation on a properly prepared screen of zinc sulphide."

In a second paper (immediately following the one just referred to) they proceeded to measure the charge (e) carried by an α-particle and gave reasons for believing that the previous measurements by Thomson and others was too small. Finally they arrived at the following results:—

Charge carried by a hydrogen atom	$= 4{\cdot}65 \times 10^{-10}$ electrostatic units.
" " an α-particle .	$= 9{\cdot}3 \times 10^{-10}$ " "
Mass of the hydrogen atom . .	$= 1{\cdot}61 \times 10^{-24}$ gram
Number of atoms in 1 gram hydrogen	$= 6{\cdot}2 \times 10^{23}$
" molecules of any gas at N.T.P. per c.c.	$= 2{\cdot}72 \times 10^{19}$
Atomic weight of α-particle . .	$= 3{\cdot}84$
" " " helium . .	$= 3{\cdot}96$

And they say:

"Taking into account the probable experimental errors in the values of $\frac{e}{m}$ for the α-particle, we may conclude that *an α-particle*

is a helium atom, or to be more precise, *the α-particle, after it has lost its positive charge, is a helium atom.*"

If these conclusions are correct, it follows that the first change which the radium atom experiences is

$$\text{Ra} = \alpha\text{-particle (later He)} + \text{Emanation (Em)}.$$

and in round numbers so far as the masses of these are concerned,

$$\underset{226}{\text{Ra}} = \underset{4}{\text{He}} + \underset{222}{\text{Em}}$$

The question now arises: Why, if this is the true explanation of what occurs, is not helium found immediately in the gas remaining after the emanation has been pumped off along with it and the emanation frozen out? If emanation and helium are produced in equi-molecular amounts from radium and immediately, the helium would certainly not have escaped the notice of a man like Ramsay, but all who have worked at the subject appear to have observed the production of helium only after an interval of one day at least.

One or other of two explanations may be suggested, namely:

(1) It may require time for the α-particle to lose its extra charge and to pass into helium.

(2) The helium produced along with the emanation may have passed into the glass of the vessels used, and so have escaped detection, and only when more of the gas was produced by the decay of the emanation was it in sufficient amount to overcome this source of error.

The first of these explanations seems the more probable.

APPENDIX.

A very curious experience of Ramsay and Gray with regard to the emanation may here be mentioned and may be given in their own words.

"In November, 1907, the Imperial Academy of Science of Vienna was so kind as to lend one of us a relatively large quantity of what

professed to be radium bromide of approximate purity. This sample, as well as two others, was dissolved in water, in three bulbs, all of which were sealed to a Töpler pump, and use was made continuously of the emanation mixed with the decomposition products of water. The total amount of radium, as metal, was 0·2111 gram, and it produced about 25 c.c. of mixed oxygen and hydrogen every week. Much of the specimen from Vienna was insoluble in water, and was found to consist largely of the carbonate.

"On December 20th, 1907, some hydrobromic acid was introduced into the bulb containing the large quantity of radium; the insoluble matter all dissolved with effervescence. For some months after this, bromine was evolved, and attacked the mercury of the pump. It ceased to appear in April, 1908. After that, the evolution of explosive gas was regular, until November, 1908. On November 11th, the normal amount of gas was produced; on that day an apparatus, constructed of lead and paraffin, containing a mixture of mercuric chloride and ammonium oxalate, was placed by Dr. Flaschner close to the 'Vienna bulb.' On November 18th there was 'remarkably little gas—about 10 c.c.' On November 25th there were 'only a few c.c.' Suspecting that a stoppage in the tap had occurred, air was admitted into the pump, the tap and tubes were cleaned, but there was no sign of a stoppage. The apparatus was again pumped to a vacuum and left. On November 30th only half a cubic centimetre was collected. On December 7th about the same quantity, and on the 14th and 18th no greater amount was collected. On that date Dr. Flaschner removed his apparatus, and after some hours replaced it refilled. The emanation was not drawn after this until January 11th, three weeks later; 8 c.c. of explosive gas were collected. On that date Dr. Flaschner finally removed his apparatus. On January 18th, 1909, 25 c.c. of gas—the old amount—were pumped off, and since then that volume has been collected weekly.

"Experiments have, however, been made to try to reproduce the inhibiting conditions. First, the bulbs were surrounded with beakers containing the actinometric mixture employed by Dr. Flaschner; next, each bulb was placed in a lead cup, more than ⅛-in. thick; third, the lead cups were paraffined on their interior, and filled with the solution already referred to; and last, the identical apparatus used by Dr. Flaschner in his experiments, and charged as in these latter, was placed as nearly as possible as he had placed it.

But all to no purpose; 25 c.c. of gas can be pumped off each week. We have failed to reproduce the conditions.

"We are absolutely certain as regards the facts, and we are also convinced that there has been no mistake. *Something* inhibited the action of the radium on water for a month and a half. Whatever that was, it was coincident in time with the presence of an apparatus placed outside the bulbs; when that apparatus was removed, the inhibition ceased. It may be remarked that the whole apparatus is in a locked room"

CHAPTER VIII

THE NEWER CHEMISTRY.

RADIO-ACTIVITY (*continued*)—EMANATIONS, PART II.—GRAY AND RAMSAY'S SECOND RESEARCHES ON THE RADIUM EMANATION—DISINTEGRATION PRODUCTS OF RADIO-ACTIVE ELEMENTS.

IN 1910—1911, Gray and Ramsay[1] returned to the subject of the atomic weight of the emanation, which they now determined from its gaseous density.

As the volume of the emanation at their disposal was, as in their previous experiments, only about $\frac{1}{10}$ cubic mm., the weight of which is some $\frac{1}{1400}$ mg. it is obvious that in order to weigh this minute quantity with sufficient exactness, a balance turning with a load not greater than $\frac{1}{100000}$ mg. was a necessity.

The construction of such a balance had been accomplished by Steele and Grant[2] of the University of Melbourne, and a brief account of it may be given. Its construction together with the principles involved are as follows:

A beam of extraordinary lightness (about half a gram) constructed of thin silica rods fused together and provided with a silica knife edge rests on a finely polished rock crystal plate. A small mirror is attached to the beam at a right angle to it, and the movements of the beam are indicated by the displacement of the reflection of a ray of light thrown on to this mirror from the filament of a Nernst lamp and received on a screen at a distance of several feet from the mirror. The object to be

[1] *Proc. Roy. Soc.*, London, Series A, Vol. 84, p. 536.
[2] *Ibid.*, Series A, Vol. 82, p. 580.

weighed is suspended along with a small sealed silica bulb containing a definite volume of air at known temperature and pressure, this bulb having been previously counterpoised by a silica weight fused to the other extremity of the beam. The balance is enclosed in an airtight box provided with glass sides, and this box can be evacuated by a mercury pump, the pressure being read by a delicate manometer. The *rationale* of the method of weighing is as follows: if a quartz bulb be filled with air at the same temperature and pressure as the air surrounding it, the effective weight of the contained air will, in accordance with the Archimedean principle, be zero; if, however, the density of the air within the bulb differs from that of the surrounding air, then the inside air will possess a certain positive or negative weight which can readily be calculated.

Thus, in Steele and Grant's micro-balance of the type they called A, the internal volume of the quartz bulb was 0·0085 c.c. It was sealed at 23° C. and 759 mm.

The weight of the air which it contained was 0·01012 mg. A change of pressure of 1 mm. in the balance case corresponded with a variation of the effective weight of

$$\frac{0{\cdot}01012}{759} = 0{\cdot}0000133 \text{ mg.} = 1{\cdot}3 \times 10^{-5} \text{ mg.}$$

and an alteration of 1° C. at 20 mm. pressure with a variation of less than 1×10^{-6} mg. The temperature effect they say is therefore negligible at all pressures lower than 50 mm., and the variation in volume of the quartz bulb with varying pressure and temperature is also negligible.

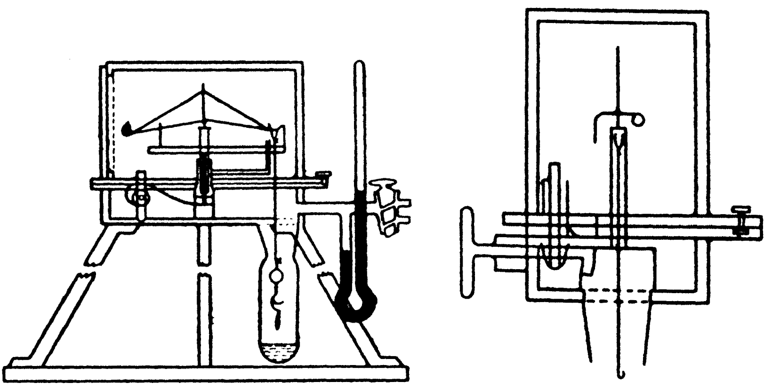
As the pressure can be read to $\frac{1}{10}$ mm., an accuracy of determination of $1{\cdot}3 \times 10^{-6}$ mg. (*i.e.*, to about one millionth of a milligram) can be obtained, provided that the zero of the instrument remains constant and the beam homogeneous.

A general idea of the construction of this balance will be

gathered from the two diagrams given below, one showing a front view of the instrument and the other a side view.

Ramsay and Gray introduced certain improvements into this form of balance, and any object lighter than 0·027 mg. or 27,000 μ mg. (millionth. milligram) could be weighed with an accuracy of 3·55 μ mg. Their present instrument, they state in their paper, is still more sensitive, weighing to 2 μ mg.

The emanation, which they now term "Niton," was treated



A B

FIG. 28.—The micro-balance. A. Front view. B. Side view.

in much the same way as in their 1909 experiments; that is to say, the purified gas was forced into a fine capillary tube of about 1 mm. internal diameter, drawn out above to a sealed point, frozen there by surrounding it with a cone of liquid air, and traces of hydrogen (along with a minute amount of niton) removed by the pump.

The tube was then sealed about 20 mm. below the tip, carefully cleaned, and placed in a little quartz "bucket," suspended from one end of the micro-balance and the weighing completed. Afterwards the tip of the density tube was broken off, all splinters being collected in the bucket; both bucket

and tube were then returned to the balance, and the air exhausted from its case; air was then again admitted and a second time exhausted. In this way, the gas (niton) was removed from the tube and replaced by air.

"Before experimenting with the precious niton, the method was tested with the less valuable xenon. Before freezing the gas, its volume was measured; it amounted to 0·0977 cub. mm. at 0° C. and 760 mm. It was then frozen and the density tube was sealed off and placed in its bucket on the balance. After breaking the tip, the pressure change was 17·1 mm. (70 − 52·9). The temperature change was too small to affect the result. This pressure change corresponds to an apparent loss of weight of 608 μ mg."

After making various corrections the following result was obtained:—

Calculated weight 577 μ mg.
Ascertained „ 578 „ „

The agreement is so precise that Ramsay and Gray remark that it is doubtless a coincidence.

"With niton, two sources of error made their appearance. In the first place, the density tube became strongly electrified and attracted dust particles and adsorbed air, and in the second, the tube was always at a higher temperature than the surrounding atmosphere during weighing, and convection currents were liable to be set up in the air surrounding one limb of the balance."

The first of these effects (which could not be entirely eliminated) was considerably reduced, as regards dust, by filtering the air before admission into the balance case through a long column of cotton wool, and secondly by burning off the dust attracted to the density tube after suspension from the beam of the balance, with a small ("pin-point") non-luminous flame, while the second effect was reduced as far as possible by weighing at a low pressure.

The exact volume of niton in the density tube was ascertained by means of its γ-ray activity, compared with that of

the original amount pumped off from the radium bulbs (after explosion of the accompanying mixture of hydrogen and oxygen and a period of several hours thereafter, in order to accumulate the quick-change products), and also compared with that of the niton pumped off along with hydrogen from the frozen gas, after a suitable interval.

As a rule, this latter, *plus* that of the gas in the weighing tube, were together equal to the total initial radio-activity of the niton before it had been purified. It was found, however, that some of the niton had entered the walls of the weighing tube and this fraction was estimated by determining the radio-activity of the empty tube, immediately after it had been weighed.

"As the quick-change products A, B and C are short-lived and change rapidly into D, and as D is a solid, it remains in the density tube and is not weighed, but the helium resulting from the change of niton into A, A into B, and C into D, escapes for the most part along with the niton; its weight must be calculated, and that of the escaping gas diminished by its amount, in order to arrive at the true weight of niton. Five experiments were made in order to determine the total loss of weight on opening the density tube, and a sixth to obtain an estimate of the helium produced by the disintegration of the niton as far as radium D."

This last was of the most elaborate description and the result obtained remarkable, as the calculated weight of the helium was 38 μ mg., whereas that actually obtained (partly by direct weighing and partly by measurement of the volume of a portion of the helium from which the weight was calculated) was 35 μ mg.—a difference of only about 10 per cent.

The lowest result of the atomic or molecular weight of niton which was obtained was 218, and the highest 227. The mean was 223.

The theoretical number, in accordance with the equation

$$Ra = He + Nit.$$

is 222·4.

(For details of one complete experiment made by Gray and Ramsay on the density of niton, see the appendix to this chapter.)

It may now be a suitable time to summarise the changes which probably occur in the radio-active elements, and in this connection the following tables may be given.

It will be seen from them that the number of what may be called "transient" elements is at least 30 (including radium, but excluding uranium and thorium), a very material addition to the list of elements.

The changes of the radio-active elements is in most cases associated with the liberation of energy in the kinetic form, and thus the study of electrical discharges in high vacua, but more especially of radio-activity has introduced important changes in certain of our views, which a few years ago were regarded as fundamental.

The more important of these are perhaps the following:

(1) The so-called chemical atoms are no longer regarded as indivisible particles, but as assemblages of much smaller particles of a common constituent.[1]

(2) In certain cases, at all events, transmutation is possible, that is to say, a given element can be transformed or transforms itself, into others.

(3) A totally unexpected source of energy has revealed itself in this "atomic disintegration"; certain "atoms" of higher weight disengaging energy (as heat or electricity, or both), when their constituents are partly expelled and partly rearrange themselves into an atom or atoms of lower weight. We shall see presently how large this source of energy may be.

A consideration of these new discoveries and views leads to the question: Are any of our so-called elements absolutely

[1] See Chapter IX., in which these views are explained, while it is also shown that there are reasons for doubting that atoms are solely composed of electrons.

URANIUM, THORIUM AND ACTINIUM WITH THEIR DEGRADATION PRODUCTS.

Element.	Atomic Weight.	Average Life Period.	Nature of Emitted Rays.	Chief Properties of Element.
Group 1.				
Uranium 1	238·5	7×10^9 years	α	The ordinary salts of uranium (uranyl salts) give a precipitate with ammonium carbonate, *soluble* in excess. They also dissolve in ether.
Uranium 2	—	$1{\cdot}4 \times 10^6$ years?	α	Non-separable from Ur 1.
Uranium Y[1]	—	2·16 days	β	Separated from uranium salts with ferric hydroxide; exists in small quantity, probably branch product from Ur 2.
Uranium X	—	35·5 days	β, γ	Also separated from uranium salts by ferric hydroxide and barium sulphate. Produced from Ur 2. Salts soluble in water, but *not* in ether. Aqueous solutions give a precipitate with ammonium carbonate, *insoluble* in excess.
Ionium	—	$3{\cdot}5 \times 10^5$ years?	α	Chemical properities of thorium from which it is non-separable.
Radium	226·4[3]	2,880 years	$\alpha, \beta, (\beta)$[2]	Salts resemble those of barium, but the sulphate and bromide are less soluble. Imparts a crimson colour to flame of Bunsen's burner.
Emanation (Niton)	222·4	5·55 days	α	Gas boiling at – 62° C. and solidifying at – 71° C. chemically inert.
Radium A	—	4·32 minutes	α	Behaves as a solid, carries positive charge, volatile in hydrogen at 400° C and in oxygen at about 550° C.
Radium B	—	38·7 minutes	$\beta, (\beta), \gamma$	Metal, volatile at about 400° C. in hydrogen, separated in pure state by recoil from Ra A, also by volatilisation and by electro-chemical methods, precipitated on zinc.
Radium C	—	28·1 minutes	α, β, γ	Separated from solution of deposit on nickel plate, volatile in hydrogen at about 430° C. in oxygen at about 1000° C.
Radium C_2	—	2·0 minutes	β	Obtained by recoil from pure Ra C, present in small quantity, probably branch product.

[1] Ur Y, Ra C_2, and Th D_2 are *branch* products, *i.e.*, the line of descent to the following product is not through them.
[2] (β) signifies β rays of very low velocity, and as a consequence easily absorbed.
[3] See p. 117 for atomic weight of radium as determined by Hönigschmid.

URANIUM, THORIUM AND ACTINIUM WITH THEIR DEGRADATION PRODUCTS—*continued.*

Element.	Atomic Weight.	Average Life Period.	Nature of Emitted Rays.	Chief Properties of Element.
Group 1—*contd.*				
Radium D (radio-lead)	—	23·8 years	β, (β)	Grey and metallic looking. Soluble in strong acids. Volatile below 1,000° C. ? Always separated from uranium minerals with lead, no methods of separating from lead yet known.
Radium E	—	7·2 days	β, γ	At first this was thought to be complex, but later work has contradicted that supposition. Separated from solutions of Ra D on nickel or by electrolysis.
Radium F (Polonium)	—	196 ,,	α	Deposited on bismuth. Volatile at 1,000° C.? Probably allied to Bi and Te. Separated from Te by hydrazine hydrate, which precipitates the latter only. Polonium may then be separated with $SnCl_2$.
Inactive Product[1] (Lead ?)	—	—	Rayless	
Group 2.				
Thorium	232·5	$1·9 \times 10^{10}$ years.	α	Hydrate insoluble in ammonia. Forms a characteristic compound with acetyl-acetone, which can be distilled *in vacuo.*
Mesothorium 1	—	7·9 years	Rayless	Cannot apparently be separated from Ra, behaves like a metal of the alkaline earth series.
Mesothorium 2	—	8·95 hours	β, γ	Behaves like a metal of the earth, or rare earth series. Mesothorium 2 can be separated from mesothorium 1 by adding a trace of zirconium chloride to the mixed solution and then ammonia when it is precipitated along with zirconia while 1 remains in solution.
Radiothorium	—	2·88 years	α	Resembles thorium. Precipitated by ammonia.
Thorium X	—	5·27 days	α	Hydrate soluble in ammonia; remains when this solution is evaporated and calcined. Resembles a metal of the alkaline earth series.
Emanation	—	78 seconds	α	Inert gas of high molecular weight (220 ?). Condensed at *minus* 120—150° C.
Thorium A	—	0·20 seconds	α	Concentrates on cathode surface.

Group 2—contd.				
Thorium B	—	15·3 hours	β (β)	Can be volatilised from a wire at a red heat (below 700°) and collected as a sublimate. Remains dissolved on treating acid solution with animal charcoal.
Thorium C_1	—	84·6 minutes	α, β	Less volatile than B, but volatilises at 1,200° C. Absorbed from an acid solution by animal charcoal.
Thorium C_2	—	?	α	
Thorium D	—	4·47 minutes	β, γ	Obtained by recoil. More easily soluble in acids and more volatile than any other of the thorium disintegration products.
Inactive Product[1] (Bismuth ?)	—	—	Rayless	
Group 3.				
Actinium	—	Unknown	Rayless	Probably a branch product at some point of uranium series. Allied to lanthanum. Hydrate insoluble in ammonia. May be partly separated by fractional crystallisation of nitrate with magnesium or manganese nitrate, when it accumulates in mother liquors.
Radioactinium	—	28·1 days	α, (β)	Separates with sulphur on adding a thiosulphate to an acid solution.
Actinium X	—	14·7 days	α	Hydrate insoluble in ammonia. Resembles in other respects Th X.
Emanation	—	5·6 seconds	α	Gas, probably of inert family. Liquid at *minus* 100—143° C. Remarkably short lived.
Actinium A	—	0·0029 seconds	α	Acts as a single product with the emanation. Analogous to Ra A.
Actinium B	—	52 minutes	(β)	More volatile than Ac C. Soluble in acids. Not removed from solution by animal charcoal.
Actinium C	—	3 minutes	α	Less volatile than Ac B. Soluble in acids. Not removed from solution by animal charcoal.
Actinium D	—	6·8 minutes	β, γ	Can be prepared by recoil. Soluble in acids. Alone removed from solution by animal charcoal.
Actinium E (unknown)	—	—	Rayless	

[1] It is important to note that the atomic weight of radium is in agreement with that which should result from the loss of three α-particles from uranium, as shown in the above scheme. Thus $238·5 - (3·99 \times 3) = 226·5$. Similarly the inactive product in the first group may eventually prove itself to be lead (At. Wt. 207·1), for Ur − 8 α-rays $= 238·5 - (3·99 \times 8) = 206·6$, and this has to some extent been supported by the analysis of certain uranium and lead minerals which show that the ratio of lead to uranium is in fair agreement with such a supposition.

PARALLELISMS EXISTING IN THE RADIO-ACTIVE SERIES.

FIRST GROUP.				SECOND GROUP.				THIRD GROUP.			
Substance.	Atomic Weight (Approx.).	Life.	Rays.	Substance.	Atomic Weight (Approx.).	Life.	Rays.	Substance.	Atomic Weight (Approx.).	Life.	Rays.
				Mesoth. 1	228	7·9 years	Rayless	Act	226·5		Rayless
Ur X	230·5	35·5 days	β, (β), γ	Mesoth. 2	228	8·95 hours	β, γ				
Ionium	230·5	3·5 × 10^5 yrs. ?	α	Rad. Th.	228	2·88 years	α	Rad. Act.	226·5	28·1 days	α, (β)
Ra	226	2,880 yrs.	α, β, (β)	Th X	224	5·27 days	α	Act X	222·5	14·7 days	α
Ra Em	222	5·55 days	α	Th Em	220	78 secs.	α	Act Em	218·5	5·6 secs.	α
Ra A	218	4·32 mins.	α	Th A	216	·20 secs.	α	Act A	214·5	·0029 sec.	α
Ra B	214	38·7 mins.	β, (β), γ	Th B	212	15·3 hours	β, (β)	Act B	210·5	52 mins.	(β)
Ra C	214	28·1 mins.	α (β), β, γ	Th C and Th C_2	212 212	84·6 mins. very short	α, β α	Act C	210·5	3·0 mins.	α
Ra C_2 (branch product)	210 ?	2·0 mins.	β	Th D (branch product)	208	4·47 mins.	β, γ	Act D	206·5	6·8 mins.	β, γ

Elements in horizontal lines emit, in nearly every case, the same kind of rays.

The atomic weights of corresponding substances in first and second groups always differ by 2, and for second and third by 1·5.

The relative lengths of the lives of the substances in the different groups alter correspondingly.

Ra C would appear to be complex. It is probable that another product, which has been called Ra C^1 by Fajans, intervenes between Ra C and Ra D, and emits α-rays.

A change of 2 in the valency occurs when an α-particle is emitted, *e.g.*, Ionium (IV.), Ra (II.), Ra Em (O), Ra A (VI.), Ra B (IV.).

Substances which emit an α-particle can most easily be separated electrolytically.

The valency rises by 1 when a β-particle is emitted, *e.g.*, Th. (IV.), Mesoth. 1 (II.), Mesoth. 2 (III.), Rad. Th. (IV.), Th. X (II.), etc.

Elements with same valency are very difficult to separate, *e.g.*, Th Io, Rad. Th.; Ra B, Ra D. Pb.

stable, or are all or at least the majority of them undergoing "degradation"?

It cannot be said that any very definite answer can as yet be given to this question, but it may be remarked that only something like a half of the known terrestrial elements have been detected in the sun, while on the other hand, it may be argued that the fact of there being so many as that at such a high temperature, indicates that their stability is considerable.

Returning, however, for a moment to the radio-active elements, whence did radium originate?

The "half-life" of that substance is some 2000 years, or in other words, a kg. of radium, if weighed now (1913), would in the year 3913 weigh half a kg. and Rutherford has calculated that in 26,000 years it would be reduced to 1 mg.

Now, as the geologists believe that the sun must have shone on the earth in such a way that animal life has been possible for the past 100 million years, it seems improbable that any radium could have existed in pitchblende so long ago as that. The question arises: Does an examination of the mineral throw any light on the origin of radium?

It contains uranium, an element of higher atomic weight than radium, which changes, though slowly, into uranium X. In 1903 Rutherford and Soddy[1] advanced evidence to show that uranium changed to radium and Soddy[2] stated in 1905, that he had proved that uranium salts changed, though very slowly into those of radium, a statement which was at first challenged, but afterwards confirmed. Boltwood[3] in 1906 separated the intermediate product which at first he thought was actinium.[4] Rutherford[5] a year later showed that

[1] *Phil. Mag.*, V., pp. 441—445, 1903.
[2] *Phil. Mag.*, VI., 9, p. 768, 1905.
[3] *Nature*, November 15, 1906; *Amer. Journ. Sci.*, 1906, 22, 537.
[4] The relative quantities of uranium and actinium in minerals are such as would exist if actinium were a branch product and not one obtained in the main line of descent.
[5] *Phil. Mag.*, VI., 14, pp. 733 to 749, 1907.

ordinary actinium preparations contain a new substance which is transformed slowly into radium and can be separated chemically from both radium and actinium. Boltwood re-examined his original preparation and found that it was this new substance and he suggested the name (ionium) for the new element.

It seems evident that a wide field has been opened up for both chemical and physical investigation in tracing the changes and examining the products of such changes among the radio-active elements.

It would also seem desirable to very carefully examine compounds of the non-radio-active elements under the most varied conditions, and especially those with high atomic weights with the view of tracing possible changes in them.

For after all, two or three thousand years, or even as many millions, are but an instant in relation to eternity, and it is by no means inconceivable, as suggested above, that all our so-called elements are undergoing slow change.

APPENDIX

SOME DETAILS REGARDING GRAY AND RAMSAY'S EXPERIMENTS ON THE DENSITY OF NITON.

In order that an idea may be formed of the operations and calculations involved in the determination of the density of niton, the following full description may be given of one complete experiment, which is taken from Gray and Ramsay's paper.

"Volume of niton accumulated in 8 days = equilibrium quantity × fraction surviving = 0·127 × 0·763 .	=	0·0969 cub. mm.
γ ray activity of this sample divisions per hour	=	3996 divisions.
γ-ray activity of fraction pumped off . .	=	353 „
Hence amount pumped off	=	0·0082 cub. mm.
Amount of niton in weighing tube = 0·0969 − 0·0082	=	0·0887 „
The weighing tube was then counterpoised on the balance.		

Pressure in balance case	= 54·4 mm.
Zero on scale of beam of light reflected from mirror	155 mm.
Twenty-five hours after drawing, the weighing-tube was broken. The gas pumped out, however, was not the original 0·0887 cub. mm., but that volume multiplied by the decay factor for 25 hours, 0·828, viz. .	0·07347 cub. mm.
Pressure in balance case after breaking the density tube	34·7 mm.
Pressure change = 54·4 − 34·7 . . .	= 19·7 mm.
Zero on scale after breaking	= 154 mm.
Difference of zero = 155 − 154 = 1 mm. .	
But from measurement 10 mm. pressure = 77 scale divisions ; hence 1 division = 10/77	= 0·13 mm.
This must be added to the pressure, 19·7 + 0·13	= 19·83 mm.
The counterpoise bulb contained 0·0270 mg., or 27,000 μ mg. of air. Its buoyancy was altered by (19·83/760) × 27,000 . .	= 703·8 μ mg.
But air entered the tube when it was broken ; the volume of the density tube ascertained by previous calibration was 0·522 cub. mm.	
Weight of this air at 34·7 mm. and 17° C, = 0·522 × 1290 × 35/760 × 273/290	= 29·2 μ mg.
The sum of these quantities, 703·8 and 29·2	= 733·0 μ mg.

"But the pressure was changed by 19·8 mm. ; this alters the weight of the density-bulb by the weight of air corresponding to the difference in volume between the glass density-bulb and a silica one. As already described, this quantity was determined directly by replacing the air bulb by a solid counterpoise of silica and using the density-bulb as a measure of buoyancy. For 19·8 mm. the "glass displacement" is equivalent to − 32·8 μ mg. A further correction has to be made, viz., the change of buoyancy due to the volume occupied by the gas itself. The volume of the density tube was 0·522 cub. mm. ; the change of pressure was 19·8 mm. ; hence the weight of this air for 19·8 mm. change = 0·522 × 1290 × 19·8/760 × 273/290 = 16 μ mg. This is a positive correction. The weight, 733 μ mg., must be diminished by the difference between 32·8 and 16, say 17 μ mg. The remainder is 716 μ mg.

"The last correction to make, is the subtraction of the weight of the helium produced by the decay of the emanation during its stay in the weighing-tube. Now :—

> 22,400 cub. mm. niton weigh, say, 222·5 mg., and
> 0·0224 cub. mm. niton weighs, say, 222·5 μ mg.

Each atom of niton gives three atoms of helium ; hence, helium from 0·0224 cub. mm. niton weighs 12 μ mg. The volume of emanation decayed in the weighing-tube is 0·0887 cub. mm. $-$ 0·0735 cub. mm. $=$ 0·0152 cub. mm., and the weight of three times that volume of helium is 8 μ mg. One quarter of this has entered the glass and has not escaped ; hence, the helium removed weighed 6 μ mg. That number deducted from 716 leaves 710 μ mg. as the weight of the niton.

"To return for a moment to its volume. The amount of niton in the weighing-tube was 0·07347 cub. mm. at the moment of pumping out. But some niton had penetrated its walls and was not removed by the pump. That amount was estimated by comparing the γ-radio-activity of the weighing-tube after it had been weighed "empty" with that of the gas pumped off, which had of course diminished in radio-activity ; this diminution corresponded with the time which elapsed since the last reading, and was measured to verify the constancy of the electroscope. The radio-activity of the residue left in the weighing-tube, was after correction for natural leak 17 divisions per hour. The original radio-activity of the niton in the weighing-tube was 3996 $-$ 353 $=$ 3643 divisions per hour ; its volume in the weighing-tube when decay commenced was 0·0887 cub. mm. ; hence the "volume" left in the tube by the retention of niton in the walls was (17 $\times$ 0·0887)/3643 $=$ 0·0005 cub. mm. This subtracted from 0·07347 cub. mm., the volume of niton in the tube at the moment of pumping out, leaves 0·0730 cub. mm. as the volume actually weighed.

"All the data are now complete ; 0·0730 cu. mm. of niton at 0° C. and 760 mm. pressure weighed 710 μ mg. A litre weighs 9·727 grams. ; a litre of oxygen weighs 1·429 ; and the molecular weight of niton is therefore 218."

CHAPTER IX

THE NEWER CHEMISTRY

RADIO-ACTIVITY (*continued*)—EXPLANATION OF OLDER FACTS AND LAWS ON THE NEW BASIS.

The subject of radio-activity is not only of interest on account of the remarkable phenomena connected with it, but also from the fact that considerations arising out of it may, and very possibly do, give a clue to the inner meaning and causes of certain fundamental properties of the so-called "atoms" of our chemical elements, such as their position in the electric series, mechanism of their union with each other, nature of valency, etc.; and light may also be thrown on the causes of the relationships embodied in the periodic law. It should however be stated that since the introduction of the ideas, a brief account of which will be given in this chapter, considerable doubt has been thrown upon them as originally propounded—and that to a large extent by the work of Sir J. J. Thomson, who, along with Larmor and Lorentz, originally developed the idea that an atom, far from being an indivisible particle, is a complicated structure consisting of electrically charged particles in rapid movement either of an oscillatory or orbital nature.

A brief note will be given at the end of this chapter as to the reasons for at least some of the doubts which have arisen in connection with the subject.

Cathode ray, electrons or corpuscles-particles, and the β rays given out in radio-active changes are, as we have seen, minute particles of matter about $\frac{1}{1700}$ the mass of a hydrogen atom,

carry charges of electricity, and only differ from each other in their velocities,[1] the cathode ray particles moving less rapidly than the so-called β rays.

Now, as cathode rays are produced when all substances are submitted to electrical discharges in high vacua, it was suggested, as a necessary consequence, that the so-called "atoms" of all substances are made up of aggregates of these particles associated in some way with corresponding charges of positive electricity. And on this view, if the charges of the latter were not carried by particles of a different material (an idea which is rather difficult to grasp), the atoms of the chemical elements differ from one another only in the number and arrangement of the electrons, or in other words that atoms are aggregates of a common constituent, which is the underlying idea of Prout's hypothesis. (See p. 49.)

But how are we to picture to ourselves these new atoms?

The electron carries a definite charge of negative electricity, and since with any charge of electricity we always associate an equal charge of the opposite kind, we should expect the negative charges on n electrons (n being the number of these in the atom) to be associated with a corresponding amount of positive electricity.

The physicists who have given their attention to this matter tell us that the simplest conception of an atom from this point of view is that of a sphere of uniform positive electrification, and exerting as a consequence a radial electric force, proportional at any point to the distance from the centre, or the positive electric force may be supposed to act from the centre of the sphere, the electrons moving about inside the latter.

The sphere will be very large in relation to the size of the electron—and Lodge has compared, in this respect, the

[1] The reader is referred to p. 125 for the relationships between rapidly moving electrified particles and their apparent masses.

former with a church in relation to grains of sand representing the latter.

Now it is obvious that, following the ordinary laws of electrically charged bodies, the electrons will mutually repel each other, while on the other hand they will be attracted to the centre of the sphere by its positive electrification.

The electrons are thus acted upon by two forces in opposite directions, and the question arises, how will they arrange themselves under these circumstances? The question can be attacked mathematically, as was done by J. J. Thomson, or if the particles are at rest, experimentally also.

The latter was done in a most ingenious way by Mayer, and some of his results are easily shown.

A number of ordinary sewing needles are magnetised in such a way that all their points, if suspended horizontally say, would point to the north, and all their eyes to the south, or the reverse. Each needle is passed through a little cork disc in such a manner that when placed in a dish of water it will float vertically with the point up. Several needles placed in the dish will repel, and therefore float away, from each other. But now if the pole of a magnet (or better that of an electromagnet) be placed beneath the dish, using such pole as will attract the eyes of the needles, the latter will be acted on by two forces in opposite directions, and will group themselves in geometric arrangements, the particular nature of which will depend upon their numbers. This is shown in Fig. 29.

It will be seen that two arrange themselves in a line, three in an equilateral triangle, four in a square; with five there are two arrangements, namely, a pentagon, and a square with a central needle.

Next, as the number of needles increases, we get an inner and an outer grouping, the former being a repetition of the grouping of the same number of needles alone. Thus, nine

arrange themselves in an outer heptagon with an inner line of two, ten in an outer heptagon, with an inner triangle; eleven also into an outer heptagon, while within it is a symmetrical group of four arranged in a square.

With an increasing number of needles, the number of rings increases; thus, nineteen arrange themselves into an inner group of two, outside of which comes a ring of seven, and outside that again a ring of ten.

Suppose now that instead of magnetised needles we have

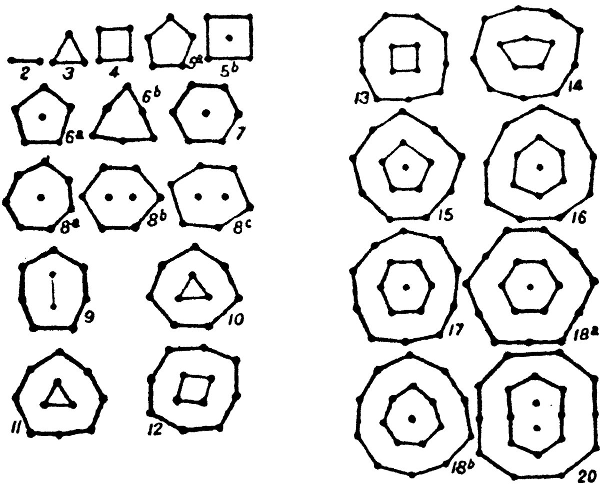


FIG. 29.—Mayer's diagram of arrangements assumed by floating magnets, under the influence of a central attractive force.

charged particles and they are not at rest, but in a state of steady motion and describing circular orbits round the centre of a sphere, the effect of the centrifugal force will be to drive them further away from the centre of the sphere, without, in many cases, destroying the character of the configuration. This is not, however, always the case. Thus, four particles, if rotating rapidly, are in stable steady motion when at the corners of a square, the plane of the square being at right angles to the axis of rotation. When, however, the velocity of

rotation of the particles falls below a certain value, the arrangement of four in one plane becomes unstable, and the particles tend to place themselves at the corners of a regular tetrahedron, which is the stable arrangement when the particles are at rest.

On the basis of a movement of the particles or electrons in rings, J. J. Thomson has calculated for certain numbers of these particles, or electrons, the groups into which they would distribute themselves, and one set of his results may be given here:—

Number of particles	60	55	50	45	40	35	30	25	20	15	10	5
Number in rings	20	19	18	17	16	16	15	13	12	10	8	5
	16	16	15	14	13	12	10	9	7	5	2	
	13	12	11	10	8	6	5	3	1			
	8	7	5	4	3	1						
	3	1	1									

The two figures shown on the Plate (Fig. 30) are actual photographs of magnetised needles passed through (blackened) cork discs and floating vertically as described above; but the arrangement was not quite the same as Mayer's.

A covered wire was coiled several times round the glass dish in which the magnets floated, the coil being at the surface of the water, so that one set of poles of the needle magnets was above and the other below the coil.[1] The current was then passed through this wire coil in such direction as to give the horizontal component of the magnetic force on both poles acting towards the centre of the dish. These forces replace those due to the action of the large magnet in Mayer's method on the magnetised needles, but in this arrangement we have the advantage that the forces act on both ends of the needles towards the centre and in such a

[1] This arrangement was suggested by Dr. A. W. Stewart.

way as to prevent the tilt of the needles which the former method causes. Thus the inter-action of the current and the magnetism of the needles gives the force towards the centre, while the repulsive force from the centre is due to the action of the magnetised needles on each other.

A shows the general arrangement, with the dish, coil, and six needles in the field, while B shows the configurations assumed by three, eleven, and twenty-four needles respectively.

It will be seen that the inner triangular grouping is common to all three.

Döbereiner's triads.—In the introductory remarks on the subject of the Periodic Law, it was mentioned that Döbereiner in 1829 noticed that in certain groups of analogous elements there were numerical relationships among their atomic weights. Thus, in certain sets of three elements in which the members of each set are closely related in their chemical properties, the atomic weight of the intermediate member is in each case very nearly the arithmetical mean of the other two.

Thus :—

Ca.	Sr.	Ba.
Cl.	Br.	I.
S.	Se.	Te.
Li.	Na.	K.

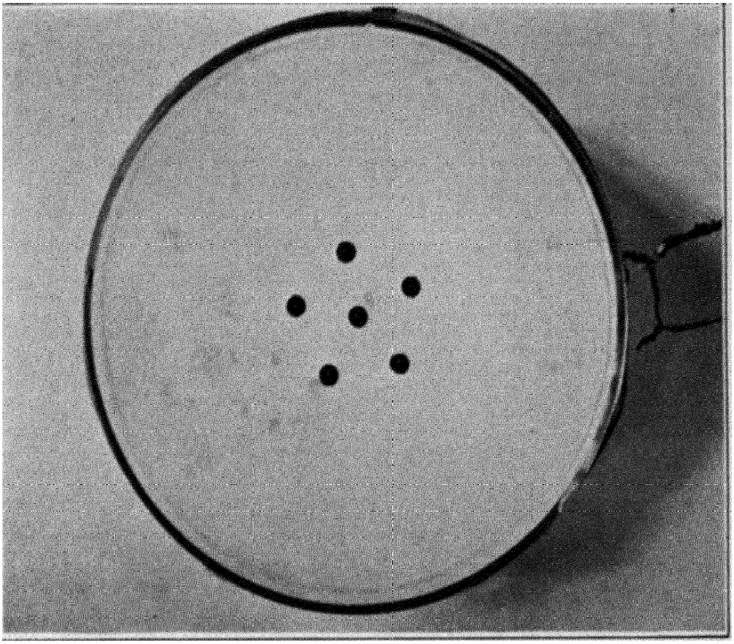
$$Sr = \frac{Ca + Ba}{2} = 88{\cdot}72 \text{ (Mean). True At. Wt.} = 87{\cdot}63$$

$$Br = \frac{Cl + I}{2} = 81{\cdot}19 \quad ,, \quad ,, \quad ,, \quad 79{\cdot}92$$

$$Se = \frac{S + Te}{2} = 79{\cdot}78 \quad ,, \quad ,, \quad ,, \quad 79{\cdot}2$$

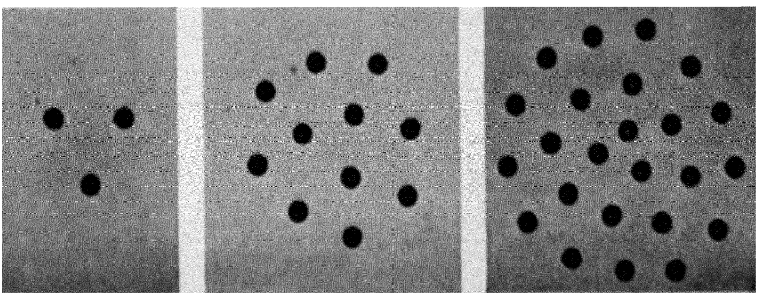
$$Na = \frac{Li + K}{2} = 23{\cdot}02 \quad ,, \quad ,, \quad ,, \quad 23{\cdot}00$$

Now take the arrangements of electrons as calculated by Thomson, numbering 30, 15, and 5 respectively. It will be



A

General arrangement.



B

Groupings of 3, 11 and 24 floating magnets showing inner triangular configuration in each case.

FIG. 30. Photographs of fl[illegible] under the influence of a magnetic force driving them towards the centre of the vessel containing them.

seen on reference to the table that in each ring there are either 5 or n $\times$ 5. Now the mean of 30 and 5 is 17·5 which approximates to 15.

The Groups in the Periodic Law.—Speaking broadly, we know that similarity of structure induces similarity in properties, and this is specially observed in organic compounds. Thus, all primary alcohols contain the group $R-CH_2OH$, in which R is frequently C_nH_{2n+1}. The following are therefore strictly analogous and closely resemble each other in properties:—

$$H - CH_2OH$$
$$CH_3 - CH_2OH$$
$$C_2H_5 - CH_2OH$$
$$C_3H_7 - CH_2OH$$

Etc.

Now what kind of similarity in atoms composed of groups of electrons, arranged in a certain number of rings (or possibly shells), might be expected to produce similarity in properties? The answer seems fairly evident, similarity in configuration.

Take the arrangements:—

Number of electrons	3	10	20	35
Number in rings	3	3	3	3
		7	7	7
			10	12
				13

Here the triangular configuration disappears after 3, but reappears with 10, when it is associated with 7, and again appears also associated with 7 in 20 and once more in the same way with 35.

Suppose now that certain properties were associated with this triangular configuration, we should have a repetition of these with atomic weights 10, 20 and 35 (Atomic Weight of

electron = 1), which is just the kind of effect we observe among the members of the same groups in the periodic law.

The series (Periods) in the Periodic Law.—But how, on the electronic theory of the nature of atoms, can the facts be accounted for which are embodied in Mendeléef's statement that :—

> "First the properties of the elements become modified as their atomic weights increase, then they repeat themselves in a new period."

The suggestions on this point we also owe to Sir J. J. Thomson. He calculated how groups of electrons varying in number from 59 to 67, which includes the entire series having an outer ring of 20, and all containing 5 rings, would arrange themselves, and found the following :—

Number of electrons	59	60	61	62	63	64	65	66	67
Number in rings	20	20	20	20	20	20	20	20	20
	16	16	16	17	17	17	17	17	17
	13	13	13	13	13	13	14	14	15
	8	8	9	9	10	10	10	10	10
	2	3	3	3	3	4	4	5	5

Now Thomson shows mathematically that in the group of 59 the number of electrons inside the ring of 20 is only just sufficient to make the ring stable. For that reason, an electron is easily detached from it, and if that occurs, the remainder of the atom becomes electro-positive. But there are now 19 electrons in the outer ring, the whole number being 58, and Thomson shows that such is a very stable arrangement, and that no more electrons could escape from it. On the contrary, they would be attracted; the addition of one, again forming the unstable group of 59.

An atom of this kind would therefore be neither positive

nor negative, but electrically neutral, like one of the inert elements.

With the next group of 60 electrons we have a more stable arrangement. While on the one hand it may lose electrons, it will not, on the other, lose them so easily as the group of 59. Hence it will not so readily assume a positive charge, but whereas the group of 59 *minus* 1 electron is totally unstable, that of 60 *minus* 1 electron has a certain degree of stability.

The group of 61 will, for similar reasons, be less electro-positive than that of 60, and that of 62 less again.

With a further increase in the number of electrons in the neutral atom, there is a greater probability of adding electrons to the atom than of liberating them, in which case the latter would receive a charge of negative electricity, and behave as an electro-negative element. Nevertheless electrons might have been expelled from the neutral atom, and hence an atom may be either electro-negative or electro-positive, but, in general, it possesses the one characteristic more strongly than the other. Now the electro-negative character predominates.

This character would increase up to 66 electrons, where the addition of 1 electron only would be possible, for then maximum stability would be reached. Such grouping would correspond with a strong electro-negative element like chlorine.

A neutral atom having 67 electrons has already maximum stability, and an electron could not be added to it. Hence again an inert element has been reached, though not of the same nature as that of 59 electrons, for these correspond to the extremes of stability and instability.

A great change occurs with the addition of another electron, as the outer ring now contains 21 of these, and such arrangement is unstable, like the group of 59, and would have similar properties.

To sum up we have the following:—

59 Electrons.	Unstable. Easily losing 1 electron and as readily gaining it again. Electrically neutral, like neon.
60 ,,	Unstable, but not so easily losing 1 electron. When, however, this is lost, it is not readily regained. Strong electro-positive element, like sodium.
61 ,,	Similar, but can lose 2 electrons. Weaker electro-positive element, like magnesium.
62 ,,	Similar, but can afford to lose 3 electrons. Weaker electro-positive element, like aluminum.
63 ,,	Quite different and can now gain as many as 4 electrons. Weak electro-negative element, like silicon.
64 ,,	Can gain 3 electrons. Stronger electro-negative element, like phosphorus.
65 ,,	Can gain 2 electrons. Stronger electro-negative element, like sulphur.
66 ,,	Can gain 1 electron. Strong electro-negative element, like chlorine.
67 ,,	Maximum stability. Electrically neutral, like argon.

We thus see that radio-activity gives a satisfactory explanation of the periodic law.

Chemical Combination.—The view that chemical attraction is of an electrical nature is not a new one, Berzelius having been the first to suggest that the forces which bind the atoms together in compounds are electrical in their origin, while both Davy and Faraday held similar views, and so also Helmholtz later.

But it does not appear that any of these attempted to

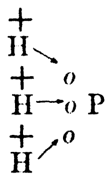
account for the fact that different elements have different valencies, on a purely electrical hypothesis. If Thomson's beautiful conceptions are true, we not only find an explanation of the facts embodied in the periodic law, but also an explanation of the facts of valency.

According to Thomson's views, an element is electro-positive if it can lose electrons and electro-negative if it can gain them under the circumstances of chemical action. Valency finds its explanation in the number of electrons which an atom can thus lose or gain.

Thus we may picture a compound such as potassium chloride as

$$\overset{+}{\mathrm{K}}\rightarrow o\ \overset{-}{\mathrm{Cl}} \text{ arising from } \overset{\text{neutral}}{\mathrm{K}} \text{ and } \overset{\text{neutral}}{\mathrm{Cl}}$$

and phosphuretted hydrogen as



in which o = an electron.

An element is neither electro-positive nor electro-negative, like argon, when it can neither lose nor gain electrons permanently, and then as a consequence it has no valency. As before said, the configuration of a group of electrons in motion is not necessarily the same as for the group at rest, and in the former case there will be a critical velocity of the electrons greater than which a certain configuration is alone stable. When the velocity diminishes below this critical value, instability sets in, and a kind of convulsion or explosion occurs, accompanied with a great diminution of the potential energy of the system, with a corresponding increase in its kinetic energy, which may be sufficient to detach considerable

numbers of electrons from the original assemblage. This apparently is what occurs in radio-active changes.

Take radium for example. Its constant disengagement of kinetic energy is shown by the heat which it radiates, while α-rays are expelled (eventually to form helium) and the rearranged electrons form the emanation. The emanation in its turn rapidly loses kinetic energy and soon explodes—so to speak—into radium A and α-rays, and similar changes occur later with radium A, etc.

The immensity of the store of energy thus locked up in our so-called atoms is shown by a calculation of Thomson's which indicates that the energy thus stored in a gram of hydrogen amounts to

$$1{\cdot}02 \times 10^{19} \text{ ergs.}$$

—an amount sufficient to lift a million tons through a height exceeding 100 yards.

This stored up energy is proportional to the number of electrons in the atom, and therefore to the atomic weight, so that it is prodigious in the case of an element like uranium.

Simple and indeed fascinating as the idea is that atoms are made up solely of matter in the form of electrons, there appears to be, as was indicated at the commencement of the chapter, a feeling which seems to be fairly general that the theory is untenable, at least in its original form.

From spectroscopic and other evidence it would appear to be certain that electrons are universal constituents of atoms, but on the other hand there seems to be no sufficient evidence for the assumption that electrons are the sole constituents of these atoms. Indeed, in 1906 Sir J. J. Thomson, who (as already stated) had so much to do in originating the electronic theory of matter, himself brought forward experimental evidence against that view, at least in its original form.

It would not be advisable, nor does the author feel himself to be competent, to discuss this very important matter at length,

but it may be stated that the three methods then (1906) apparently available for throwing light upon the question and all developed by Thomson, depending on

(1) The penetrating power of the electron (β-ray) into matter;

(2) The scattering of Röntgen rays by gases;

(3) The dispersion of light by gases;

appear to have led to much the same result, namely, that all but about one thousandth of its mass is associated with the positive part of an atom, which would tend to show that an altogether exaggerated rôle has been attached to the electron in the constitution of matter.[1]

[1] See art. "Radio-activity," *Chem. Soc. Annual Reps.*, 1906, p. 350.

CHAPTER X

THE NEWER CHEMISTRY

THE QUESTION OF INORGANIC EVOLUTION—LOCKYER'S VIEWS AND WORK.

We have seen that in the case of the radio-active elements a process of "degradation" is occurring, whereby those of higher atomic weight are slowly giving rise to others of lower atomic weight, and arguing from the special to the general, it may at least be suggested that all the elements are slowly undergoing change.

But, it may be asked, how can that be, without their exhibiting radio-activity?

If such changes are actually occurring, the answer may possibly be, either :—

(1) That certain changes are in point of fact rayless, *e.g.*, actinium into radio-actinium, meso-thorium 1 into meso-thorium 2, or—

(2) That the rays emitted escape detection. Such was the case with the very "soft" β-rays (*i.e.*, having very low velocities) escaping when radium B changes into radium C, radium D into radium E, etc.

But whether all the elements are changing or not, some certainly are, and the question naturally arises, is the opposite kind of process occurring anywhere in nature?

In other words, is there side by side with the degradation of the elements a process of their evolution occurring?

Degradation, as we have seen, is accompanied with a disengagement of energy, part of the potential energy of the

more complex atom becoming liberated as kinetic energy, while the rest remains locked up in the simpler atom or atoms which result from the change.

Consequently evolution, should it occur, ought to involve the opposite, namely, the absorption of kinetic energy and its conversion into the potential form.

And therefore it seems only reasonable to search in hot regions for signs of inorganic evolution; and as such hot regions are to be found in the sun and stars, it again seems only reasonable to appeal to them for possible information on the subject. Researches on this matter have formed the chief work done by Sir Norman Lockyer during more than forty years of his life, he tells us,[1] and he was one of the first of our modern scientific men to indicate the possibility of our so-called elements being compounds.

> "For twenty years I longed for an incandescent bottle," he says, "in which to store what the centre of the (electric) spark produces. The stars have provided it."

Needless to say, the only instruments of service in direct investigations of the kind were then, and still are, the spectroscope and telescope combined. But indirectly others were of service, and notably such as could be used for the production of very high temperatures, like those of the electric arc and spark.

When Lockyer first took up the work, the belief was general that an element could have one and only one spectrum. But the "one element, one spectrum" notion was quite erroneous, and Plücker, with Hittorf, in 1865, was able to announce that

> "there is a certain number of elementary substances which, when differently treated, furnish two kinds of spectra of quite a different character, not having one line or band in common."

The difference in character to which reference is here made consists in the spectrum produced at the lower temperature

[1] "Inorganic Evolution."

being composed of flutings, which are replaced by lines when the higher temperature is reached.

It is easy to demonstrate a change in the spectra of certain substances produced by changes in the temperature of their vapours.

Thus sodium, at the temperature of an ordinary Bunsen's burner, gives a spectrum consisting only of two lines close together in the yellow part and corresponding with the D Fraunhofer lines. Whereas the arc spectrum of the same metal is much more complex and shows quite a number of lines of different colours and notably in the green and red region.

For spectroscopic work we have at our disposal the following sources of heat :—

Source.		Average temperature, degs. C.
(1) Bunsen's burner	Ordinary . . about	1,500
	Méker (Base of flame) ,,	1,700
(2) Oxy-hydrogen blowpipe . . .	,,	2,000
(3) Electric arc	,,	3,500—3,900 ?
(4) High potential spark . . .	,,	8,000—9,000 ?

Long and short lines.—If we regard the arc or spark as a cylinder or globe of flame, it is obvious that the inside will be the hottest and densest and the outside the coolest and rarest. The idea occurred to Lockyer of examining arc or spark spectra in such a way that the image of the source of light was thrown on to the slit of the spectroscope by a lens, the spark or arc being placed horizontally and the slit vertically, as shown in Fig. 31.

He observed in the case of several metals three sets of lines corresponding with the three ranges of temperature.

"Here then was the first glimpse of the idea that the complete spectrum of a chemical element, obtained at the highest temperature, might arise from the summation of two or more different line spectra

produced at different degrees of temperature, and therefore bringing us in presence of two or more molecular complexities, that is, different molecules broken up at different temperatures."

Lockyer also made a careful study of spectra produced at the very highest temperature he could obtain, namely a 40-in. spark from an induction coil combined with a powerful condenser. By this means he found in the spectra of many

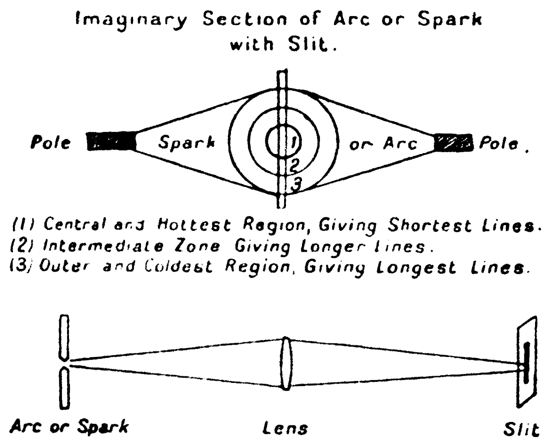


FIG. 31.

elements new or intensified lines, which he called "enhanced lines."[1]

The nature of the spectrum of iron at different temperatures is as follows:—

(1) Flame spectrum (oxy-hydrogen blowpipe flame). A few lines and flutings only, including several well-marked lines, some of them arranged in triplets.

(2) The arc spectrum, consisting, according to Rowland, of 2,000 lines or more.

[1] The work of Hartmann, Fabry and Buisson, Hemsalech and others has shown that these lines are also obtained from certain parts of flames and arcs, and hence temperature alone does not explain their existence, but they must also depend on chemical or electrical conditions.

(3) The spark spectrum, differing from the arc spectrum in the enhancement of some of the short lines and the reduced relative brightness of others.

(4) A spectrum consisting of a relatively very small number of lines, which are intensified in the spark.

Before considering the bearing of these different spectra on solar phenomena it will be advisable for us briefly to consider the constitution of the sun.

Nature of the Sun.[1]—The sun, a mere fiery globe as it appears to us, has a diameter approaching a million miles (actually 865,000) and is made up of several parts.

The main mass probably consists of intensely hot and strongly compressed gases.

The question of the temperature of the sun and of the stars generally is one of considerable interest. The methods for estimating these temperatures are based upon an examination of the light radiating from them, but unfortunately that light, as it reaches us, is not necessarily purely that of the original source, but is often modified by its passage through the dust or vapours surrounding the glowing mass of the luminary; hence there would appear to be considerable uncertainty as to the actual temperatures of the sun and other stars.

One of the methods for these temperature measurements depends upon what is known as "Wien's Law of Displacement" and is based upon the wave length of that colour which corresponds with the maximum of heat in the spectrum of the hot body (which should be a normal spectrum). The application of this law is very simple and is expressed by the equation

$$T = \frac{2{\cdot}89}{\text{W.L. in mm.}}$$

in which T is the (absolute) temperature, to be calculated in

[1] This description is to a considerable extent taken from Arrhenius' work, entitled "Worlds in the Making."

centigrade degrees, and W.L. the wave length of that line in the spectrum which corresponds with the highest temperature.

The average temperature of the sun as thus calculated is

$$\frac{2{\cdot}89}{0{\cdot}00055} = 5{,}255 \text{ (absolute)}$$

or a little under 5,000° C.

Another method is based upon the total radiation of the hot body, which is proportional to the 4th power of the absolute temperature. This is called "Stefan's Law of Radiation" and with it the solar temperature has been estimated at about 6,200°.

Arrhenius tells us however that various other estimates have been made.

Wilson and Grey found for the centre of the sun at first a temperature of 6,200° which they afterwards corrected to 8,000°. Le Chatelier arrived at a figure for the sun itself of 7,600°.

Carrington and Hodgson saw certain solar clouds or *faculæ* break out on a certain occasion from the edge of a sun spot, which were five or six times as bright as the sun's photosphere and corresponding according to Arrhenius with a temperature of from 10,000—12,000° C. a temperature, he tells us, in all probability above the critical point of any of the chemical elements.[1]

It may be mentioned that the temperature of white stars such as Sirius and Vega has been found (by means of the radiation method) to be some 1,000° higher than that of the sun, while on the other hand that of the red star, Betelgeuse, would appear to have a temperature some 2,500° lower than that of the sun. Prodigious temperatures are spoken of later on by Arrhenius in his book "Worlds in the Making" as existing during the formation of suns from nebulæ when their tempera-

[1] The critical temperature (abs.) is, according to Arrhenius, usually about 1½ times the boiling point (abs.) at atmospheric pressure.

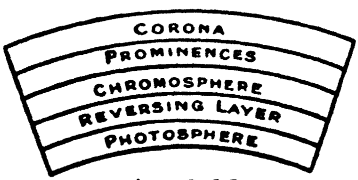
ture is rising, as high a figure as 71 *million degrees* being mentioned in this connection, but presumably as a matter of calculation only.

The density of the solar mass is about 1·4 times that of water, so that the general body of the sun should in physical properties resemble that of a viscid liquid, which would account for the stability and persistence of sun spots.

The sun being of this nature in its main or inner mass, cooling must occur in the incandescent gases expelled from it as they recede outwards, and expand, causing effects to some extent analogous to those occurring in our own atmosphere, such as the formation of lower and higher clouds, with an upper atmosphere above these consisting largely of attenuated gases.

Unlike the clouds of our terrestrial atmosphere, however, those of the sun consist of incandescent particles of carbon and liquid particles of metals; while, for reasons to be given later, there is strong reason for believing that the outermost (or highest) layers of the solar atmosphere contain, in addition to attenuated gases, dust, or minute solid particles.

The outer layers of the sun may be represented diagrammatically thus:—



[This diagram, however, must not be regarded as more than a rough approximation, the different layers no doubt merging into each other.]

Photosphere. This presents a granulated appearance, which has been compared with that of a greyish white cloth, almost hidden by snowflakes, the so-called *faculæ* (torches) corresponding with the latter. (See Fig. 32.)

The *faculæ* are believed to be clouds of rising incandescent vapours, like our terrestrial clouds, except that the latter are cold, and consist of water spherules, or minute ice crystals. The *faculæ*, as before mentioned, are believed to be composed

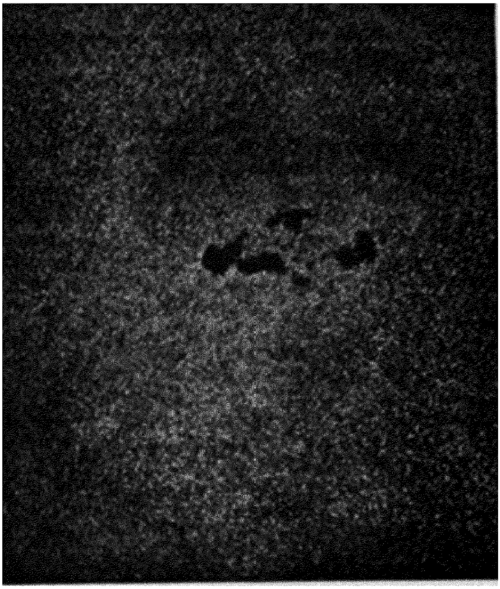


FIG. 32.—Sun spots and *Faculæ*.
(Reduced from Arrhenius' "Worlds in the Making.")

of solid particles of carbon and liquid particles of molten metals, such as iron, magnesium, calcium and sodium. The smallest *facula* we are able to see is probably at least 130 miles in diameter.

In the neighbourhood of the *faculæ* are occasional dark spots, the so-called "sun spots," which were discovered as early as 1610. The number and size of these change from year to year in a somewhat irregular way, the period amounting on an average to a little over 11 years. The maxima in these spots seem to be in relationship with the maxima observed in certain terrestrial phenomena, such as:

(1) Polar lights (Auroræ).

(2) Magnetic variations.

(3) Cirrus clouds (though to a lesser extent).

Sun spots are believed to consist of huge vortices of descending gases, with rising temperature, which are therefore "dry," and do not carry any clouds with them.

Reversing layer. This consists of vapours at a lower temperature than those of the photosphere, and therefore external to it. The following elements (in the order of their atomic weights) have been recognised in it.

(1)	(2)	(3)	(4)
H	Si	Co	Sn
He	K ?	Ni	Ba
C	Ca	Cu	Ce
N	Ti	Zn	Platinum metals
O	V	Sr	Pb ?
Na	Cr	Mo	U
Mg	Mn	Ag	
Al	Fe	Cd	

less than one-half the known terrestrial elements.

Chromosphere. This is only visible to the naked eye during a solar eclipse (the disc of the moon then screening off the

intense light of the photosphere). The chromosphere corresponds with our highest terrestrial atmosphere, and in addition to incandescent metallic vapours in its lower portions, contains hydrogen and helium in its upper parts, causing these to shine with a pink or a purple glow.

The thickness of the chromosphere is estimated as being from 5,000 to 6,000 miles, less than $\frac{1}{100}$ of the solar diameter. From the chromosphere rise rays of fire, which have been compared with blades of grass rising from a meadow. When these flames rise higher, say to 9,000 miles, they are called "prominences."

Prominences. The number and altitude of these grow with sun spot maxima. Some prominences are called "quiet" and others "metallic."

The latter consists of masses of gases and incandescent vapours ejected from the solar interior with enormous and almost incredible velocities, amounting at times to over 500 miles *per second*, whereas our wildest terrestrial hurricanes very rarely have a wind velocity of 100 miles *per hour.* While the average height of the solar prominences is about 32,000 miles, they often exceed that figure, one having been observed almost as high as the sun's radius, *i.e.*, over 400,000 miles. The quiet prominences consist almost exclusively of hydrogen and helium, but sometimes contain traces of metallic vapours. They resemble clouds floating in the solar atmosphere.

Beyond (that is to say above) the chromosphere, yet another luminous zone appears in the sun, namely, the so-called *corona.*

Corona. This consists of streamers of pearly light, which may extend beyond the sun's disc, a distance of several solar diameters, and therefore for a million or two of miles. The appearance of the corona varies with the maximum and minimum sun spot periods. During the former the streamers are fairly uniformly distributed round the sun's disc, but

during the latter they extend like huge brooms from the equatorial parts, like the lines of force about the poles of a magnet. It is therefore supposed that the sun acts as a magnet, the poles of which are situated near the sun's geographical poles. At times of moderate sun spot frequency the streamers seem to emanate from the neighbourhood of the maximum belt of sun spots, and the corona assumes a quadrilateral shape. (See Fig. 39.)

The spectrum of the inner parts of the corona is that of hydrogen, together with lines of an element not met with terrestrially, to which the name "coronium"[1] has been given, and which seems to occur more particularly in the higher regions of the "inner corona." The spectrum of the "outer corona" is continuous, and is therefore that of reflected light, probably from solid particles ejected from the sun, as we shall learn later, by the so-called "radiation pressure."

To return to Lockyer's work:—

"Next the spectra of different parts of the sun—those of the chromosphere, prominences and spots—were compared with different parts of the light source, and core of the arc, and the centre of the spark, and the outer regions of both. . . . Wonderful anomalies were at once detected; lines known to belong to the same chemical element behaved differently in several ways. Some were limited to prominences, others to spots, and in some solar storms different iron lines indicated different velocities.

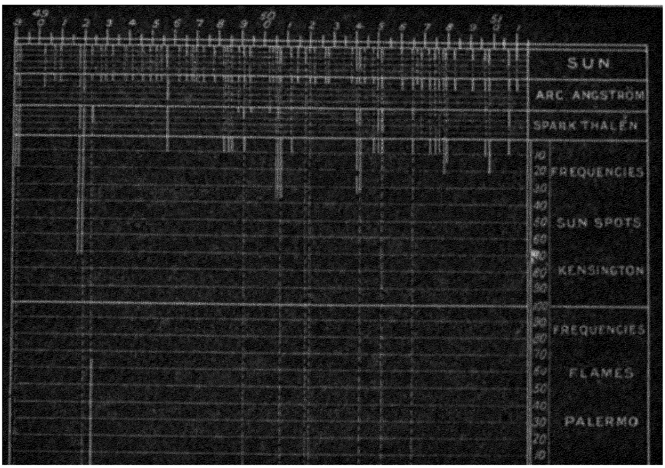
"In the spectrum of the hottest part of the sun[2] open to our inquiries, the region, namely, immediately overlying the photosphere, which I named the chromosphere, the anomalies become legion. Suffice it to say, that in the hottest part of the sun we could get at the spectrum of iron then represented in Kirchhoff's map of the

[1] The spectrum of this body consists of several bright lines; one of these of a green colour (λ 5315·9) appears to be specially characteristic. Certain Italian observers have stated that coronium occurs in the gases from the solfatara or sulphur beds at Puzzuoli. (Abs. *Chem. Soc. Journ.*, 1899, p. 482.)

[2] Lockyer is of the opinion in his work, "Inorganic Evolution," that the reversing layer is *outside!* the chromosphere, and that the latter is the *hottest* lowest stratum of the sun's atmosphere—views which are certainly not shared by a number of other workers on the nature of the sun.

ordinary solar spectrum by 460 lines was reduced to three lines. . . . observations and cross references of this kind during the next few years convinced me that the view that each chemical element had only one line spectrum was erroneous, and that the results obtained suggested that the various terrestrial and solar phenomena were produced by a series of simplifications brought about by each higher temperature employed."

And further on in the same work he draws attention to two other points relative to iron in the sun, viz., that in the



IRON SPOT LINES AT KENSINGTON CONFRONTED WITH IRON PROMINENCE LINES AT PALERMO.

FIG. 35.—(From Lockyer's "Inorganic Evolution.")

maximum sun spot periods the lines widened in spot spectra are nearly all unknown ; at the minimum they are chiefly due to iron and other familiar substances, and also that the up-rush or down-rush of the so-called iron vapour in the sun is not registered equally by all the iron lines, as it should be on the non-dissociation hypothesis.

Lockyer then goes on to say :—

"It seemed perfectly clear then, that in the sun we are not dealing with iron itself, but with primitive forms of matter contained in iron,

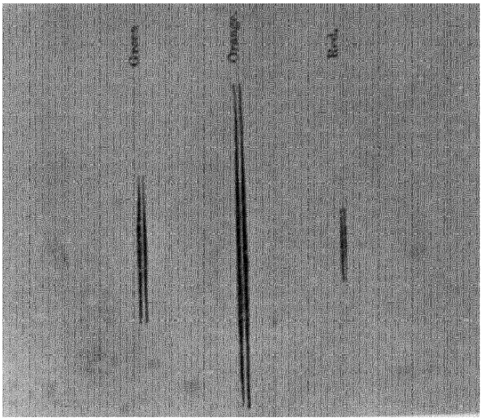


FIG. 33.—The long and short lines of sodium taken under the same conditions, showing that the orange line extends furthest from the poles. (From Lockyer's "Inorganic Evolution.")

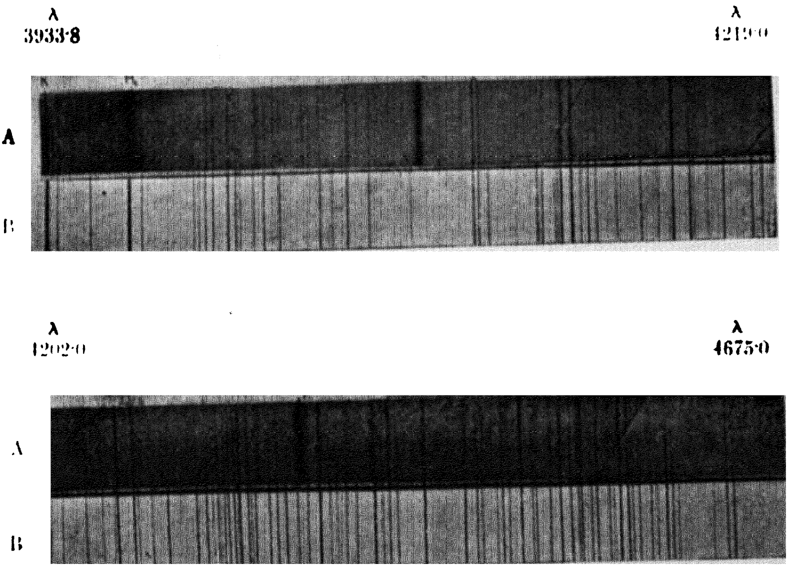


FIG. 34.—Lockyer's [illegible] trum" and the method of usi[illegible] son of α Cygni and the enhanced lines [illegible] metals ([illegible] group).

A = Spectrum of α Cygni between wave lengths stated.
B = Test spectrum of enhanced lines.
(From Lockyer's "Inorganic Evolution.")

which are capable of withstanding the high temperature of the sun, after the iron observed as such, has been broken up as suggested by Brodie."

Regarding magnesium, Lockyer found the flame spectrum to be very different from the spark spectrum. In the latter, some of the lines observed in the former disappear, while two new lines make their appearance. Now the flame lines of magnesium do not appear among the Fraunhofer lines, while some of those of the spark do.

Then in the case of calcium he also found that its arc spectrum shows a certain blue line particularly prominently, while two other lines H and K are thin. In the solar spectrum exactly the reverse is observed, H and K being thick, and the blue line thin. In solar storms the blue line is always absent, while H and K are almost always seen. Again, in eclipses the blue line is absent, while H and K are the brightest. In sun spots H and K are reversed or darkened while the blue line is not.

"Finally, then, the similar changes in the spectra of certain elements, changes observed in the laboratory, sun and stars, are simply and sufficiently explained on the hypothesis of dissociation."

Lockyer prepared a "test" spectrum as he called it. This consisted of as complete a map as he could make of the "enhanced" lines of the different elements, that is to say, of either new lines, or of old ones intensified by the great heat of the high potential spark. (See Fig. 34.)

On comparing this test spectrum with the bright lines in the sun's chromosphere (best observed at the time of a total eclipse of the sun) he found that the most important metallic lines of the latter were precisely those included in the former. From these different facts it seemed clear to Lockyer that in the hottest parts of the sun the elements are broken up into new forms of matter which he called "proto-elements." Thus, the

spectrum of calcium as it appears in the chromosphere is caused by "proto-calcium." And Pickering, he tells us, recognised some time ago a new form of hydrogen in certain stars (*e.g.* Zeta Puppis) the spectrum of which was quite different from that of ordinary hydrogen. It has since (1912) been observed by A. Fowler in hydrogen-tubes, containing helium. Lockyer speaks of this as "proto-hydrogen." When a substance is heated until it glows, its spectrum lengthens with increasing temperature. Commencing with red rays, the spectrum first extends into those which are yellow, thence to those which are green and blue, and finally into violet and ultra-violet.

Lockyer, by taking advantage of this principle in relation to what may be called "stellar thermometry," arranges the stars into three main groups, namely, those giving

(1) The longest spectrum.
(2) A medium ditto.
(3) The shortest spectrum.

When the longest spectra are examined, they are found, he says, to belong to gases chiefly, the medium spectra to metals, and in the shortest spectra carbon is indicated. Therefore, we have the following further classification :—

(1) Highest temperature, longest spectrum, gaseous stars.
(2) Medium temperature, medium spectra, metallic stars.
(3) Lowest temperature, shortest spectra, carbon stars.

A closer scrutiny of the three groups of stars led Lockyer to conclude that in:

(1) A gas of the helium family was strongly marked with faint enhanced lines.

(2) A gas of the same family feebly marked, and strong enhanced lines, or no gas of the helium family and strong arc lines.

(3) Faint arc lines.

Therefore, he says, the chemical law seems to be as follows :—

(1) In the very hottest stars we find hydrogen, helium asterium, and doubtless other gases still unknown.

(2) At the next (lower) temperatures, we find these gases becoming replaced by metals in the state in which they are observed in the laboratory, when the most powerful jar spark is employed.

(3) At a lower temperature, the gases disappear almost entirely, and the metals occur in the state produced by the electric arc.

According to Lockyer, stars were originally formed by the falling together of meteorites,[1] the temperature increasing with the condensation of the swarm up to a maximum, and then diminishing. This he represents graphically by the following diagram.

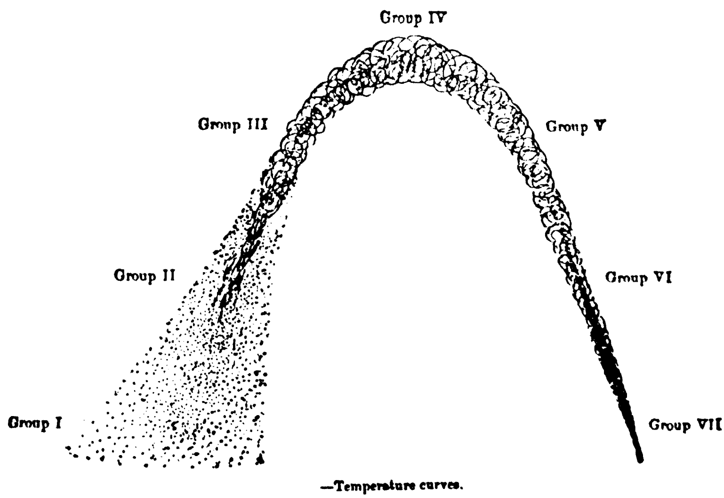


FIG. 36.—Formation of stars. (Temperature curves.) (From Lockyer's "Inorganic Evolution.")

[1] A view which, as we shall see later, is by no means universally held.

It will be seen that according to it, stars may be arranged in seven groups, groups 1, 2 and 3 undergoing condensation, and therefore rising in temperature; the maximum being reached in group 4, groups 5, 6 and 7 corresponding in temperature with groups 3, 2 and 1, but consisting of stars of falling temperature.

Lockyer gives the following list:

HOTTEST STARS.

Two stars in the constellation of Argo (ζ Puppis and γ Argus). Alnitam or Alnilam (ϵ Orionis).

STARS OF INTERMEDIATE TEMPERATURE.

Ascending series.	Descending series.
β Crucis	Achernar
ζ Tauri	Algol
Rigel	Markab
α Cygni	———
———	Sirius
Polaris	Procyon
Aldebaran	Arcturus

COLDEST STARS.

Ascending series.	Descending series.
Antares	19 Piscium
(Nebulæ)	(Dark stars),

and he tells us that the metallic lines are thickest in stars of *increasing* temperature, and the hydrogen lines thickest in stars of *decreasing* temperature.

"The stars used in the discussion give us very definite results, showing that the various chemical forms are introduced at six distinct heat levels."

He points out that the simplest chemical substances appear at the highest temperatures, and the more complex at lower temperatures. The case of carbon appears to be an exception to this rule, but while its atomic weight is low, there is reason to believe that its molecule is complex.

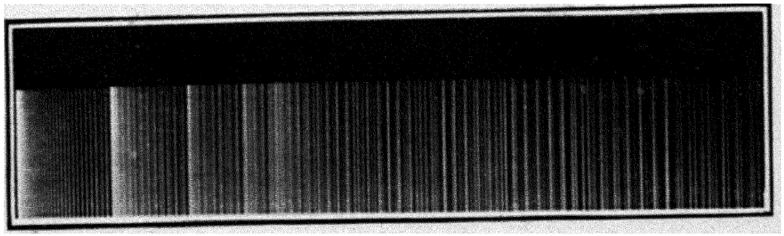


FIG. 37.—Fluted spectrum of carbon. (From a photograph by Dr. Robt. Jack.)

Lockyer then more or less leaves the question of evolution of the elements, and devotes his attention rather to arguments in favour of their composite nature. Among these is what he terms "the series evidence."

It is well known that the spectra of the elements differ in complexity. Thus, the spectra of the metals of the alkalies consist of but few lines, while the spectrum of iron for instance (at the temperature of the arc) contains, according to Rowland, some 2,000.

Can a single atom vibrate in thousands of different ways, at the same time, such vibrations corresponding with the lines of its spectrum?

Certain substances show what is called a "banded," "fluted" or "channelled space" spectrum (*e.g.*, carbon, nitrogen, cyanogen, etc.), such spectra having the appearance of a row of Corinthian columns, seen under a strong side light. (See Fig. 37.)

Under sufficient dispersion, each set of bands (*i.e.*, each column) is resolved into groups of lines. These get closer towards the red or blue end of the spectrum until they terminate in a single line, called the "head." A single band thus consists of a head and of a series of lines becoming more and more separated until they encounter another head.

A band spectrum therefore consists to a large extent of repetitions of similar groups of lines, *e.g.*, pairs, triplets, quartets, etc. But the regular distribution of the lines may be to a small extent upset by certain irregularities.

It has been found that mathematical relationships exist (1) as regards the lines starting from one head and (2) as to the distribution of the heads in the complete spectrum.

It has also been found that mathematical relationships exist as regards the groupings of lines in a spectrum, which often form series characterised by the relative strengths of the lines. Thus, the group showing the strongest lines is spoken of as the

"principal" series; that showing weaker lines as the "first subordinate" or "nebulous" series; and that showing the weakest lines as the "second subordinate" or "sharp" series.

A complicated spectrum may often be rearranged in a number of such series, each of which shows regularity of arrangement.

As an example existing in such series, the differences in the oscillation frequencies (that is, the number of waves per unit of length, or $\frac{1}{\lambda}$ where λ is a particular wave length), in three series of triplets in the spectrum of zinc, may be given :—

		Dif.		Dif.	
(1)	2,079	910	2,989	582	3,571
	Dif. 39		39		38
(2)	2,118	910	3,028	581	3,609
	Dif. 18		18		20
(3)	2,136	910	3,046	583	3,629

But not only do numerical relationships of this kind exist, but it is also possible (in certain cases, at all events) to express the lines of a spectrum series by a formula. The first to do this was Balmer, who in 1885 gave the following formula for the spectrum of hydrogen :—

$$\lambda = A \frac{m^2}{m^2 - 4} \times 10^{-6} \text{ cm.}$$

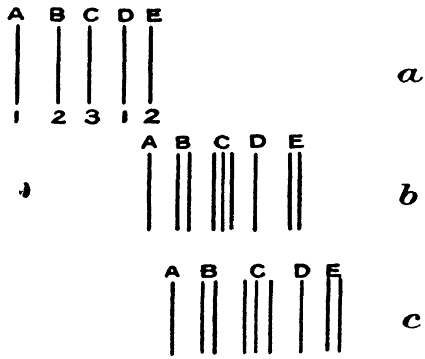
where λ is the wave length of the line to be calculated, A a constant of the value 3645, and m one of the series of numbers 3, 4, 5, etc., up to 11.

With this formula close agreement was found between the (then) known and the calculated lines of the gas, while later, when Pickering discovered in certain stars what Lockyer termed "proto-hydrogen," Balmer's formula was found to apply with equal accuracy to its spectrum.

Other formulæ for calculating spectra have been worked out by Rydberg, Runge and Paschen, Kayser, and others.

Sir J. J. Thomson may next be quoted as to how this "series" evidence, as Lockyer terms it, bears on the question of the complexity of our chemical atoms.

"As an example of a property that might very well be associated with a particular grouping of the corpuscles,[1] let us take the vibration of the system as shown by the position of the lines in the spectrum of the element. First let us take the case of three corpuscles by themselves in the positively electrified sphere. The three corpuscles have nine degrees of freedom, so that there are nine possible periods. Some of these periods in this case would be infinitely long, and several of the periods would be equal to each other, so that we should get nine different periods.



"Suppose that the lines in the spectrum of the three corpuscles are as represented in the figure, where the figures under the lines represent the number of periods which coalesce at that line; *i.e.*, regarding the periods as given by an equation with nine roots, we suppose that there is only one root giving the period corresponding to the line A, while corresponding to B there are two equal roots, three equal roots corresponding to C, one root to D, and two to E. These periods would have certain numerical relations to each other, independent of the charge on the corpuscle, the size of the sphere in which they are placed, or their distance from the centre of the sphere. Each of these quantities, although it does not affect the ratio of the periods, will have a great effect upon the absolute value of any one of them. Now suppose that these three corpuscles, instead of being alone in the sphere, form but one out of several groups in it, just as the

[1] "Electricity and Matter," p. 119.

triangle of magnets forms a constituent of the grouping 3, 10, 20, and 35 magnets.[1] Let us consider how the presence of the other groups would affect the periods of vibration of the three corpuscles. The absolute values of the periods would generally be entirely different, but the relationship existing between the various periods would be much more persistent, and although it might be modified it would not be destroyed. Using the phraseology of the Planetary Theory, we may regard the motion of the three corpuscles as being 'disturbed by the other groups.'

"When the group of three corpuscles was by itself, there were several displacements which gave the same period of vibration; for example, corresponding to the line C there were three displacements, all giving the same period. When, however, there are other groups present, then these different displacements will no longer be symmetrical with respect to these groups, so that the three periods will no longer be quite equal. They would, however, be very nearly equal unless the effect of the other groups is very large. Thus, in the spectrum, C, instead of being a single line, would become a triplet, while B and E would become doublets. A and D would remain single lines.

"Thus the spectrum would now resemble *b* in the figure; the more groups there are surrounding the group of three, the more will the motion of the latter be disturbed, and the greater the separation of the constituents of the triplets and doublets.

"The appearance as the number of groups increases is shown in *b* and *c*. Thus, if we regarded the element which contains this particular grouping of corpuscles as being in the same group in the classification of the elements according to the Periodic Law, we should get in the spectra of these elements homologous series of lines, the distances between the components of the doublets and triplets increasing with the atomic weight of the elements.

"The investigations of Rydberg, Runge and Paschen, and Kayser have shown the existence in the spectra of the elements of the same group, series of lines, having properties in many respects analogous to those we have described."

Lockyer then adduces further evidence in favour of the view that the elements are of a composite nature, such as the Zeeman effect, Crookes' meta-elements, etc.

[1] See p. 183.

CHAPTER XI

THE NEWER CHEMISTRY

THE BIRTH AND DEATH OF WORLDS—GRAVITATION AND RADIATION PRESSURES—ARRHENIUS' VIEWS.

In a remarkable book entitled "Worlds in the Making," Arrhenius takes up the questions of the creation and of the eventual destruction of stars and of worlds like our own, and gives reasons for believing that both operations are simultaneously occurring in cosmos, or, so to speak, a "winding-up" and a "running-down" of the machinery of the universe; the two chief forces at work being the mechanical pressure of light, or simply the "radiation pressure," on the one hand, and gravitation on the other.

In this chapter, as far as possible, Arrhenius' own words will be used.

The Radiation Pressure.—He tells that as early as 1746 Euler expressed the opinion that the waves of light exerted a pressure upon the body on which they fell. This was denied at the time, but was proved to be correct by Maxwell in 1873, in his great theoretical treatise on the nature of electricity. Maxwell showed that rays of heat—and the same applies, as was shown later, to radiations of any kind—must exert a pressure just as great as the amount of energy contained in a unit volume, by virtue of their radiation.

He calculated the magnitude of the pressure, and found it so small that it could hardly have been demonstrated with the experimental appliances then available. But, as we shall see presently, this was done later.

As already mentioned, Arrhenius applied the facts of the radiation pressure to the explanation of certain cosmical phenomena, and here his own words may be quoted:—

"The magnitude of the radiation pressure of the solar atmosphere must be equivalent to 2·75 mgs.—if the rays strike vertically against a black body one square centimetre in area.

"I also calculated the size of a spherule of the same specific gravity as water, such that the radiation pressure to which it would be exposed in the vicinity of the sun would balance the attraction of the sun. It resulted that equilibrium would be established if the diameter of the sphere was 0·0015 mm., provided, as was afterwards ascertained, that all light was reflected from the sphere.

"If the diameter be still smaller, the radiation pressure will prevail over the attraction, and the particle be repelled by the sun, but only up to the point where the spherule is 0·3 times greater than the wave length of the incident rays. When it is smaller, gravitation will once more predominate.

"But spherules whose sizes are intermediate between these two limits will be repelled. It results, therefore, that molecules which have far smaller dimensions than those mentioned will not be repelled by the radiation pressure, and that therefore Maxwell's law does not hold for gases. When the circumference of the spherule is exactly equal to the wave length of the radiation,[1] radiation pressure is at its maximum, and will be nineteen times as great as the attractive force of gravitation. These calculations apply to all spheres, totally reflecting the light, of a specific gravity like water, and to radiation and attraction corresponding to that of the sun. Since the sunlight is not homogeneous, the maximum effect will somewhat be diminished, and it is nearly equal to ten times the gravity for spheres of a diameter 0·00016 mm."

Effects which ought to be produced by Radiation Pressure.—It ought to be possible actually to demonstrate the effects of radiation pressure, if particles of a sufficiently small size can be obtained with a sufficiently powerful source of radiation.

This was done by Nichols and Hull, who, by heating spores of the fungus *Lycoperdon bovista*, which are almost spherical,

[1] Red, say, ·00076 mm.; violet, say, ·00039 mm.

and of a diameter of about 0·002 mm., up to a red glow, produced little spherules of carbon of an average density of 0·1.

These were mixed with emery powder, placed in a vessel shaped like an hour-glass, and the vessel and its contents exhausted as far as possible. They then caused the mixed powder to fall in a fine stream into the lower part of the vessel, while exposing it to the concentrated rays of an arc lamp at the same time. The emery particles fell perpendicularly, while the carbon spherules were driven sideways by the radiation pressure.

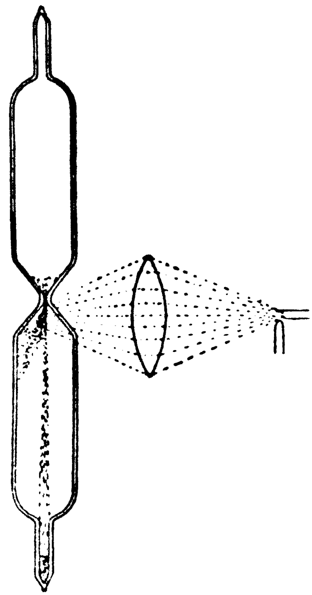


FIG. 38.—Demonstration of radiation pressure. (From Arrhenius' "Worlds in the Making.")

But apart from this actual demonstration of its effects, there ought to be, one would anticipate, cosmical phenomena caused by radiation pressure of two kinds, namely, loss of matter from hot bodies, and gain of the matter thus expelled by cool bodies. Take, for instance, the sun and the stars at intensely high temperatures. In them, we have every reason for believing, stupendous explosions occur, leading to the scattering of dust into their outer atmospheres, together with ionised gas particles. The dust particles, if of a size to be affected by the radiation pressure, will be driven into space, and approaching relatively cold masses like the earth, or more attenuated and colder masses (at least in their exterior portions), such as comets and nebulæ, will be attracted to them by the force of gravity, and electric phenomena might possibly then occur.

The following phenomena appear, in point of fact, to be related to the radiation pressure:—

(1) *Polar Lights* (*Auroras*).—These, as their name implies, occur most frequently in polar regions, attaining their maximum of frequency in circles which enclose the magnetic and geographic poles. They are of two classes, namely, (1) those without, and (2) those with streamers. The former are very quiet, and their light is strikingly constant. As a rule, these polar lights drift slowly towards the zenith, and they do not give rise to magnetic disturbances. They generally have the shape of an arch.

In polar lights of the second class, the streamers (flickering lines of light) are sometimes quite separated from each other, but, as a rule, and especially below, they melt into one another, and form so-called "draperies," which are so easily moved, and so unsteady, that they present the appearance of fluttering in the wind. The streamers run approximately in the direction of the "dip" or inclination of the magnetic needle. This class of polar lights affects the compass. When they pass the zenith, their influence on the needle changes sign, so that the deviation produced changes from east to west, as the auroral ribbon moves from north to south. It is believed that they are caused by violent displacements of negative electricity. Their frequency corresponds with sun spot maxima, when the solar eruptions are most violent and the velocity of the ejected dust particles at its greatest.

On the other hand, polar lights without streamers occur most frequently during years of sun spot minima. (See Figs. 39 and 40.)

"The rays of the corona in the neighbourhood of the poles of the sun are then laterally deflected by the action of the magnetic lines of force of the sun. The small negatively charged particles have evidently a low velocity, so that they move quite close to the lines of force in the neighbourhood of the solar poles, and are concentrated

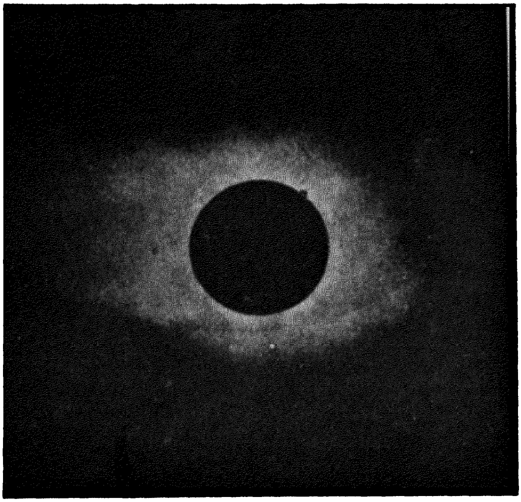


FIG. 39.—Photograph of the solar corona, 1900 (after Langley and Abbott). Illustrating the appearance of the corona in years of minimum frequency. (From Arrhenius' "Worlds in the Making.")

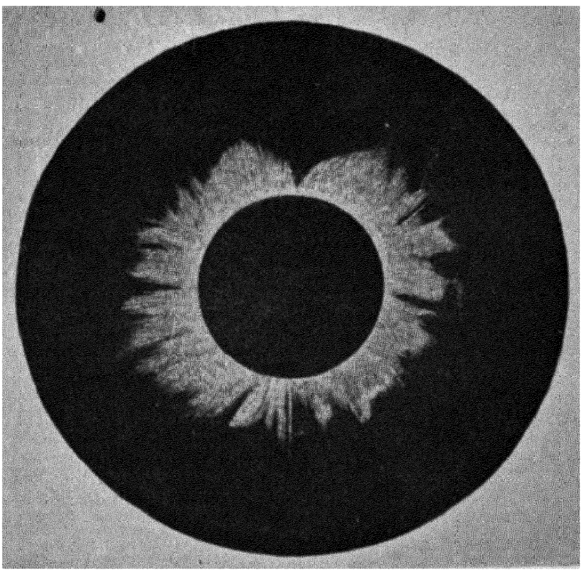


FIG. 40. Photograph of the solar corona of 1870 (after Davis). The year 1870 was one of maximum sun-spot frequency. (From Arrhenius' "Worlds in the Making.")

near its equator. There the magnetic forces are weaker, and the solar dust can therefore be ejected by the radiation pressure, and will accumulate in a large disc expanding in the equatorial plane.

"Part of this solar dust will come near the earth and be deflected by its magnetic lines of force. It is to be expected that the negatively charged particles coming from the sun will drift chiefly towards the district which is situated somewhat to the south of the magnetic north pole when it is noon at this pole. When it is midnight, most of the negatively charged particles will be caught by the lines of force before they pass the geographic north pole, and the maximum belt of auroras will for this reason surround the magnetic and geographic poles" (as appears to be actually the case).

"Where the (negatively-charged) dust collides with molecules of air, it will produce a phosphorescent glow, as if these molecules were hit by the electrically-charged particles of radium."

In the spectra of polar lights, the most intense line is found to belong to the krypton, while the other lines are those of other members of the family of inert elements, in addition to nitrogen.

Arrhenius suggests that the krypton is of solar origin.

(2) *Comets* (literally "hairy bodies") may be defined as long-tailed stars—using the word "star" in the common sense as a luminous celestial object. The *nucleus*, or bright and star-like spot, together with the surrounding "coma," or hair, are commonly spoken of as the "head" of the comet, while the "tail" presents a nebulous appearance, and may show more than one streamer.

Comets may be of enormous size, sometimes actually filling more space than the sun does, while their tails often stream out for millions of miles. Comets are very light bodies.

The spectrum of a comet consists partly of a continuous band of colours, which is probably due to sunlight reflected from small solid particles, and partly of the bands characteristic of gaseous hydrocarbons and cyanogen; these being due to electric discharges through the gases.

As a comet approaches the sun its tail lengthens, and other

less volatile bodies evaporate from its nucleus. The lines of sodium appear, and when it is very near the sun those of iron also. The ejected matter comes from that part of the nucleus which is turned towards the sun and collects in clouds, analogous to terrestrial clouds formed on a hot day. These clouds are provided with a kind of hood, which envelops like a thin semi-spherical veil that side of the nucleus which is turned towards the sun, and sometimes more than one of these hoods appear. As early as the beginning of the seventeenth century Kepler came to the conclusion that the tails of comets are repelled by the sun, and there can be no doubt that such is the case, the cause being the sun's radiation pressure acting on the minute particles forming the tail.

Bredichin, a Russian astronomer, conducted a number of measurements of the magnitude of the forces with which comets' tails are repelled by the sun, and arrived at the conclusion that these tails may be divided into three classes in which the repulsion is respectively 19, 3·5—1·5, and 1·3—1 times stronger than gravitation.

Some comets show several tails, for instance, that of Donati in 1858 (Fig. 41). They probably consist of highly attenuated clouds of particles of different sizes, and different specific gravities, the smallest and lightest of which may consist of minute particles of carbon, containing hydrogen, and formed by the carbonisation of hydrocarbons, originally present in the tail of the comet. According to Arrhenius it is conceivable that such spherules may have a specific gravity of 01 as in the experiment of Nichols and Hull, and under the most favourable circumstances experience a repulsion 40 times as strong as solar gravitation.

Comets sometimes disappear, and are converted into meteorites. Thus, Biela's Comet, which has disappeared since 1852, was rediscovered in a belt of meteorites which approaches the earth's orbit each year on November the 27th.

FIG. 41.—Donati's comet at its greatest brilliancy in 1858. (From Arrhenius' "Worlds in the Making.")

Meteorites contain in addition to the elements revealed by spectrum analysis in comets, namely,

H, C, N, Na, Fe,

the following:—

He, O, Mg, Al, Si, P, S, Cl, Ca, Ni, Co, Cr, As,

their composition strongly recalling that of the volcanic products of so-called "basic" nature. According to Arrhenius, the structure of meteorites favours the view that they have been formed by the coalescence of a multitude of extremely fine grains, and the same author is of the opinion that comets are probably formed in the spirals of nebulæ, where the cosmic dust is stopped in its motion.

Energy of the Sun.—The sun is dissipating almost inconceivable amounts of heat, corresponding yearly with 2 gram calories for each gram of its mass. If the specific heat of the sun were the same as that of water, which in that respect surpasses most other substances, the solar temperature would obviously fall 2° C. each year, and as the temperature of the outer portion of the sun is probably from 6,000—7,000°C., the sun should have cooled completely in historic times.

Geologists now believe, however, that the sun must have shone on the earth in such a way that animal life was possible for at least one hundred million years.

How then can we account for the supply of heat which the sun has lost during that time?

Various theories have been proposed. Thus, R. Mayer suggested that the sun's income of heat was derived from swarms of meteorites dashing into it. But this theory is untenable for several reasons. In the first place, it may be calculated that if the earth dashed into the sun, the heat thereby provided would only serve to maintain the sun's heat expenditure for a hundred years. Again, by their rush into the sun, almost uniformly from all sides, the meteorites would

long ago have put a stop to the sun's rotation on its axis, while the increase in its mass caused by them would shorten each of our years by nearly three seconds, which astronomers tell us is not the case—and finally, a corresponding number of meteorites would also have to fall upon the earth—and it has been calculated that thereby its surface temperature should have been raised to 800°C.

Helmholtz sought to account for the sun's income of heat by its own shrinkage, but here again calculations show that the heat thus liberated would be insufficient. Helmholtz himself, on this argument, limited the further existence of the earth (under conditions similar to those at present obtaining) to 16 million years, and if calculations are made on his data, a state like the present can only have existed for about 10 million years.

Others have suggested that the sun's expenditure of heat is due to the solar mass containing radium, and according to Arrhenius, if each kilogram of the sun's mass contained only 2 mgs. radium, "that amount would be sufficient to balance the heat expenditure of the sun for all future ages."[1]

There are, however, objections to this theory, and the views now held by Arrhenius, and apparently by others also, on the sources of the sun's heat income, are not only of a very remarkable nature, but are also in conflict with Lockyer's theory of the decomposition of the chemical elements by intense heat.

On the contrary, Arrhenius, and those who share his views, reason from the fact that heat is not necessarily a decomposing agency—the mechanical theory of heat teaching that at high temperatures substances are produced the formation of which involves an absorption of heat (endothermic compounds). Thus acetylene is formed when carbon is heated to

[1] From what has been ascertained as regards the "life" of radium, it is difficult to see how this can be the case, unless radium is being constantly produced in the sun.

the temperature of the arc (3,500—3,900° C) in an atmosphere of hydrogen, while oxygen and nitrogen combine also at the same temperature—a fact which is now taken advantage of in a (relatively speaking) new technical process for the manufacture of nitric acid.

It is also known from experience that the higher the temperature at which a compound is formed, the greater in general is the heat absorbed.[1]

A similar law applies to the influence of pressure. When the pressure is increased, such processes will be favoured as will yield products of smaller volume.

Now the spectrum of the sun's photosphere is distinguished by lines, while in that of the sun spots bands occur suggestive of compounds.

"If we imagine a mass of gas rushing down from a higher stratum of the sun into the depths of its interior, as gases do in sun spots, complex compounds will be produced by virtue of the increased pressure. This pressure must increase at an immense rate towards the interior of the sun, by about 3,500 ats. per kilometre. The gases which dissociate into atoms at the lower pressures and the higher temperatures of the extreme solar strata above the photosphere clouds enter into combination in the depths of the spots, as we learn from spectroscopic examination. Owing to their high temperatures, these compounds absorb enormous quantities of heat in their building up, and these quantities of heat are to those which are concerned in the chemical processes of the earth in the same ratio as the temperature of the sun to that at which chemical reactions are proceeding on the earth. As these gases penetrate further into the sun, temperature and pressure are still more increased, and there will result products more and more abounding in energy and concentration. We may therefore imagine the interior of the sun charged

[1] The heats of formation (negative) of a few endothermic compounds may here be given (in large calories = K):—

	K.
SbH_3	$-86{\cdot}8$
C_2N_2 (from diamond)	$-73{\cdot}9$
C_2H_2 (from diamond)	$-58{\cdot}1$
NO...	$-21{\cdot}6$

with compounds, which brought to the surface would dissociate under an enormous evolution of heat, and an enormous increase of volume.

"These compounds have to be regarded as the most powerful blasting agents, by comparison with which dynamite and gun-cotton would appear like toys."

End of the Sun.—There is evidence, as we have seen, that the sun is now a cooling star, but even when it has cooled down to the present temperature of the earth, or even lower, it will still contain, according to Arrhenius, mighty supplies of high explosives, which may make their presence manifest at a later stage in its history.

The extinction of the sun will no doubt be attended at first with phenomena such as occurred in the formation of the earth. A solid crust will eventually surround it, to be again and again burst by volcanic action, but except for the glowing lava and the gleams of the volcanic fires, all will be in darkness. Next, water will condense as clouds, and eventually oceans will form. The sun will now cool rapidly, the oceans will freeze, while later carbonic anhydride will liquefy and solidify. Later still new oceans will form of the liquefied atmospheric gases, while eventually the solar atmosphere will consist of hydrogen and helium with some nitrogen.

Birth of Suns.—When an extinct star moves forward through infinite spaces of time, it will ultimately meet another star, either cold like itself, or hot and luminous. Arrhenius calculates the probable time required for such a meeting, in the case of the sun with its present dimensions, and its present velocity through space (13 miles per second), and finds that something like a hundred thousand billion years would be required before it would collide with another star of a similar kind, or if there are a hundred times as many dark as there are luminous stars (an assumption which he says is not unjustifiable) the probable interval before the next collision may be something like a thousand billion years, during the

last 99 per cent. of which the sun will have been a cold star.

The new stars which flash up from time to time probably represent such collisions, and their spectra tell us that during the early part of their history gases issue from them with enormous velocities, while later their spectra change and become characteristic of the nebulæ. Arrhenius pictures the collision between two dark stars by the diagram given below,

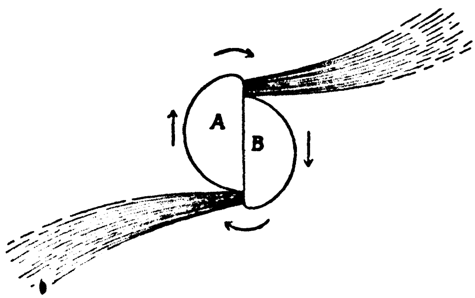


FIG. 42.—Diagram indicating the consequences of a collision between two extinct suns, A and B, moving in the direction of the straight arrows. A rapid rotation in the direction of the curved arrows results and two powerful streamers are ejected by A B, the explosive substances from the deeper strata of A and B being brought up to the surface by the collision. (From Arrhenius' "Worlds in the Making.")

with special reference to a new star in Perseus (*Nova Persei*), which flashed up on February 21-22, 1901. His description of the course of events probably taking place then is as follows:—

"At the collision, matter will have been ejected from both these celestial bodies, at right angles to the relative directions of their motions, in two powerful torrents, which would be situated in the plane in which the two bodies were approaching each other. The rotational speed of the double star, which will be diminished by this ejection of matter, will have contributed to increase the energy of ejection. We remember now that when matter is brought up from the interior to the surface of the sun, it will behave like an explosive of enormous power. The ejected gases will be hurled in terrific flight about the rapidly revolving central portions. . . . The

streams are rapidly cooled, owing to the quick expansion of the gases. They will also contain fine dust, consisting largely of carbon, probably, which had been bound by the explosive materials. The clouds of fine dust will obscure the new star more and more, and will gradually change its white brilliancy into yellow and reddish, because the fine dust weakens blue and green rays more than it does yellow and red rays."

Afterwards the double star, as its spectrum proved, became a stellar nebula.

"The continuous light of the central body has more and more been weakened by the surrounding masses of dust. By the radiation pressure, these masses are driven towards the outer particles of the surrounding gaseous envelope, consisting principally of hydrogen, helium, and 'nebular matter.' There the dust discharges its negative electricity, and thus calls forth a luminescence which equals that of the nebulæ. . . .

"We have to consider next that owing to the incredibly rapid rotation, the central mass of the two stars will, in its outer portions, be exposed to centrifugal forces of extraordinary intensity, and will therefore become flattened out to a revolving disc. . . .

"The spiral form of the outer portions of many nebulæ has for a long time excited the greatest attention. In almost all the investigated instances it has been observed that two spiral branches are coiling about the central body. . . . (See Fig. 43.)

"The nebulæ which are produced by collisions between two suns are soon crossed by migrating celestial bodies, such as meteorites or comets, which there occur in large numbers. By the condensing action of these intruders they are then transformed into star clusters. . . . (See Fig. 44.)

"Our considerations lead to the conclusion that there is rotating about the central body of the nebula an immense mass of gas, and that outside this mass there are other centres of condensation moving about the central body, together with the masses of gas concentrated about them. Owing to the friction between the immigrated masses and the original mass of gas which circulated in the equatorial plane of the central body, all these masses will keep near the equatorial plane, which will therefore deviate little from the ecliptic. We thus obtain a planetary system, in which the planets are surrounded by colossal spheres of gas. . . .

FIG. 43.—Spiral nebula in the Canes Venatici. Messier 51. Taken at the Yerkes Observatory on June 3, 1902. (From Arrhenius' "Worlds in the Making.")

FIG. 44.—The great nebula in Andromeda. Taken at Yerkes Observatory on September 18, 1901. (From Arrhenius' "Worlds in the Making.")

"In concluding this consideration, we may draw a comparison between the views which were still entertained a short time ago and the views and prospects which the discoveries of modern days open to our eyes.

"Up to the beginning of this century the gravitation of Newton seemed to rule supreme over the motions and over the development of the material universe. By virtue of this gravitation the celestial bodies should tend to draw together, to unite in ever-growing masses. In the infinite space of past time the evolution should have proceeded so far that some large suns, bright or extinct, could alone persist. All life would be impossible under such conditions.

"And yet we discern in the neighbourhood of the sun quite a number of dark bodies, our planets, and we may surmise that similar dark companions or satellites exist in the vicinity of other suns or stars; for we could not understand the peculiar to-and-fro motions of those stars on any other view. We further observe that quite a number of small celestial bodies rush through space in the shape of meteorites or shooting stars which must have come to us from the more remote portions of the universe.

"The explanation of these apparent deviations from what we may regard as a necessary consequence of the exclusive action of gravity will be found under two heads—in the action of the mechanical pressure of light and in the collisions between celestial bodies. The latter produce enormous vortices of gases about nebular structures in the gaseous condition; the radiation pressure carries cosmical dust into the vortices, and the dust collects into meteorites and comets and forms, together with the condensation products of the gaseous envelope, the planets and moons accompanying them.

"The scattering influence of the radiation pressure therefore balances the tendency of gravitation to concentrate matter. The vortices of gas in the nebulæ only serve to fix the position of the dust which is ejected from the suns through the action of the radiation pressure.

"The masses of gas within the nebulæ form the most important centres of concentration of the dust which is ejected from the sun and stars. If the world were limited, as people used to fancy, that is to say, if the stars were crowded together in a huge heap, and only infinite, empty space outside of this heap, the dust particles ejected from the suns during past ages by the action of the radiation pressure would have been lost in infinite space, just as we imagined that the radiated energy of the sun was lost.

"If that were so, the development of the universe would long since have come to an end, to an annihilation of all matter and all energy. Herbert Spencer, among others, has explained how thoroughly unsatisfactory this view is. There must be cycles in the evolution of the universe, he has emphasised. That is manifestly indispensable if the system is to last. In the more rarefied, gaseous, cold portions of the nebulæ we find that part of the machinery of the universe which checks the waste of matter, and still more the waste of force from the suns. The immigrating dust particles have absorbed the radiation of the sun and impart their heat to the separate particles of the gases with which they collide. The total mass of gas expands, owing to this absorption of heat, and cools in consequence. The most energetic molecules travel away, and are replaced by new particles coming from the inner portions of the nebulæ, which are in their turn cooled by expansion. Thus every ray emitted by a sun is absorbed, and its energy is transferred, through the gaseous particles of the nebulæ, to suns that are being formed and which are in the neighbourhood of the nebula or in its inner portions. The heat is hence concentrated about centres of attraction that have drifted into the nebula or about the remnants of the celestial bodies which once collided there. Thanks to the low temperature of the nebula, the matter can again accumulate, while radiation pressure, as Poynting has shown, will suffice to keep bodies apart if their temperature is 15° C., their diameter 3·4 cm., and their sp. gr. as large as that of the earth, 5·5. At the distance of the orbit of Neptune, where the temperature is about 50 absolute and approximates therefore that of a nebula, this limit of size is reduced to nearly 1 millimetre. It has already been suggested that capillary forces which would prevail under the co-operation of the dust grains, rather than gravity, play a chief part in the accumulation and coalescence of the smaller particles. In the same manner as matter is concentrated about centres of attraction, energy may be accumulated there, in contradiction to the law of the constant increase of entropy.

"During this conservational activity the layers of gas are rapidly rarefied, to be replaced by new masses from the inner parts of the nebula, until this centre is depleted, and the nebula has been converted into a star cluster or a planetary system which circulates about one or several suns. When the suns collide once more new nebulæ are created.

"The explosive substances, consisting probably of hydrogen and

helium (and possibly of nebulium[1] also) in combination with carbon and metals, play a chief part in the evolution from the nebular to the stellar state, and in the formation of new nebulæ after collisions between two dark or bright celestial bodies. The chief laws of thermodynamics lead to the assumption that these explosive substances are formed during the evolution of the suns and are destroyed during their collisions. The enormous stores of energy concentrated in these bodies perform, in a certain sense, the duty of powerfully acting fly-wheels interposed in the machinery of the universe, in order to regulate its movements and to make certain that the cyclic transition from the nebular to the star stage and *vice versa* will occur in a regular rhythm during the immense epochs which we must concede to the evolution of the universe.

"By virtue of this compensating co-operation of gravity and of the radiation pressure of light, as well as of temperature equalisation and heat concentration, the evolution of the world can continue in an eternal cycle, in which there is neither a beginning or end, and in which life may exist and continue for ever and undiminished."

[1] Characterised by two spectral lines, not found in any terrestrial substance. Probably a gas as difficult to liquefy as hydrogen or helium.

APPENDIX

Continuation of Collie and Patterson's Researches on the Presence of Neon in Hydrogen after the passage of the Electric Discharge through the latter at Low Pressures.

In June 1913[1] a further paper on the above was contributed, in which it was shown:—

(1) That electrodes are not necessary, for if a powerful oscillating discharge be passed through a coil of wire round a glass bulb containing a little hydrogen, helium with some neon could be detected in the residual hydrogen. The hydrogen and oxygen used in these experiments were tested in quantities up to 100 c.c., but not a trace of helium or neon was found in them.

(2) That in an apparatus where the tube through which the discharge took place was surrounded by a vacuous tube, gas was perpetually appearing in the latter and disappearing in the former, but the volume disappearing was very much greater than that appearing in the outer tube. The gas operated upon was hydrogen, and that appearing in the outer tube consisted largely of the same substance together with traces of helium and neon and a gas which gave the spectrum of carbon on sparking. The gas rapidly decreased in volume usually to about one-half and sometimes even less, the carbon spectrum then almost entirely disappearing, while the hydrogen (and the traces of helium and neon) remained. This same phenomenon almost invariably occurred when testing for helium and neon. After the residual hydrogen had been exploded with excess of oxygen, and the remainder of the latter absorbed by charcoal cooled by liquid air, the gas remaining should be

[1] *Proc. Chem. Soc.*, Vol. XXIX., No. 418, p. 217.

pure helium or neon or a mixture of the two. The spectrum, however, was always a carbon spectrum, and it was only after sparking for some time that this spectrum disappeared and the pure spectrum of helium and neon replaced it. There was always at the same time a diminution in the total volume of gas, usually over 50 per cent.

(3) The gas giving the carbon spectrum is also produced in the bulb round which a wire has been curled and through which an oscillating discharge has been passed, also in a tube containing a piece of platinum foil placed in the focus of a concave cathode of aluminum bombarded by a cathode stream, so that it becomes red-hot. At first hydrogen is given, then hydrogen mixed with helium and some neon, then less hydrogen and helium and some of the gas giving a carbon spectrum. After this apparently no more helium is produced, but an increasingly large amount of the gas giving the carbon spectrum. If this gas is sparked in contact with mercury vapour, it almost instantaneously disappears, and it was found impossible to reproduce it by heating the tube or varying the pressure in it.

(4) As it could be separated from the hydrogen in which it was found by exploding with excess of oxygen and removing that excess by means of charcoal cooled with liquid air, it would appear to be a highly uncondensable gas and not readily oxidised. That result, taken in conjunction with the fact that it gives a carbon spectrum, is very difficult to explain, and the investigators suggest that it may be the same as that discovered by Sir J. J. Thomson and called by him "X_3."

Various experiments were made with electrodes which were not aluminum, but these need not be discussed here. Finally Collie and Patterson arrive at the following conclusions:—

(*a*) Electrodes apparently are not necessary for the production of the helium and neon.

(*b*) Hydrogen in considerable quantities can be made to apparently disappear in tubes through which a heavy discharge passes.

(*c*) A gas is produced in the tubes that gives a carbon spectrum. It entirely disappears when sparked in contact with

mercury. It is not readily condensed by charcoal cooled in liquid air, nor easily oxidised by sparking with oxygen.

Finally it may be mentioned that one of the investigators was of the opinion that the metallic "splash" given by electrodes of certain metals when dissolved in aqua regia gave a precipitate with barium chloride, but it was proved later that this was due either to something dissolved from the glass or to chloride of silver precipitated on diluting the acid solution, as metallic silver had been used as a solder to unite the copper electrode to the platinum wire sealed into the glass.

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